CONTENTS

A CASE OF TIDAL WAVES ON AN OPEN SHEET OF WATER OF VARIABLE DEPTH

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[1] Various cases of surface waves in two dimensions when the depth varies according to certain specified laws, have been considered in classical hydrodynamics. We shall consider the case of tidal waves in a cylindrical basin with horizontal circular cross-section and variable depth. So far as known to me, the particular case I am treating has not been considered before.

The horizontal cross-section of the cylinder being a circle of radius $2a$, let the origin be taken to be the centre of the cross-section on the surface of water. If ζ be the height of water above the undisturbed level at the point (x, y), ho the mean depth and u and v the velocity components in the x and y directions, the equation of continuity is—

$$\frac{\partial \zeta}{\partial t} = -\frac{\partial}{\partial x} (h\, u) - \frac{\partial}{\partial y} (h\, v)$$

And the dynamical equations are

$$\frac{\partial u}{\partial t} = - g \frac{\partial \zeta}{\partial x}$$

$$\frac{\partial v}{\partial t} = - g \frac{\partial \zeta}{\partial y} \text{ and the boundary condition is } \frac{\partial \zeta}{\partial n} = 0 \text{ at } r = 2a$$

Eliminating u and v we get

$$\frac{\partial^2 \zeta}{\partial t^2} = g \left\{ \frac{\partial}{\partial x}\left(h \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial y}\left(h \frac{\partial \zeta}{\partial y} \right) \right\}$$

Assuming simple harmonic oscillations, let ζ vary as $e^{i\sigma t}$.
Then we have

$$\frac{\partial}{\partial x}\left(h \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial y}\left(h \frac{\partial \zeta}{\partial y} \right) + \frac{\sigma^2}{g} . \zeta = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \quad (1)$$

We shall consider the case when $h = h_o \left(1 + m \sin \frac{r\pi}{2a} \right) \qquad . \qquad . \qquad . \qquad . \quad (2)$

r being the distance from the origin and m being small.

Since h is a function of r only, the eqn. (1) reduces to

$$h \triangle^2 \zeta + \frac{dh}{dr} . \frac{d\zeta}{dr} + \frac{\sigma^2}{g} . \zeta = 0$$

Using (2) we get

$$\left(1 + m \sin \frac{r\pi}{2a} \right) \triangle^2 \zeta + \frac{m\pi}{2a} \cos \frac{r\pi}{2a} . \frac{\partial \zeta}{\partial r} + \frac{\sigma^2}{gho} . \zeta = 0$$

Introducing polar co-ordinates and assuming that ζ varies as $\cos (s\theta)$, this eqn. becomes

$$\left(1 + m \sin \frac{r\pi}{2a} \right) \left(\frac{\partial^2 \zeta}{\partial r^2} + \frac{1}{r} . \frac{\partial \zeta}{\partial r} - \frac{s^2}{r^2} . \zeta \right) + \frac{m\pi}{2a} . \cos \frac{r\pi}{2a} . \frac{\partial \zeta}{\partial r} + \frac{\sigma^2}{gho} . \zeta = 0$$

or $\qquad \frac{d^2\zeta}{dr^2} + P \frac{d\zeta}{dr} + Q\zeta = 0$

where $\qquad P = \frac{1}{r} + \frac{m\pi}{2a} . \dfrac{\cos \frac{r\pi}{2a}}{\left(1 + m \sin \frac{r\pi}{2a} \right)}$

$$Q = \frac{\sigma^2}{gho \left(1 + m \sin \frac{r\pi}{2a} \right)} - \frac{s^2}{r^2}$$

Let us change the dependent variable from ζ to u by the relation $\zeta = u \, e^{-\frac{1}{2}\int P \, dr}$, so that the differential equation changes to

$$\frac{\partial^2 u}{\partial r^2} + I \, u = 0$$

where

$$I = Q - \tfrac{1}{2}\frac{\partial P}{\partial r} \cdot - \tfrac{1}{4} P^2$$

$$= -\frac{s^2}{r^2} + \frac{\sigma^2}{gho}\left(1 + m \sin\frac{r\pi}{2a}\right)$$

$$+ \tfrac{1}{2}\left[\frac{1}{r^2} + \frac{m \, \pi^2 \sin\dfrac{r\pi}{2a}}{4a^2\left(1 + m \sin\dfrac{r\pi}{2a}\right)} + \frac{m^2\pi^2}{4a^2}\cos^2\frac{r\pi}{2a}\left(1 + m \sin\frac{r\pi}{2a}\right)^{-2}\right]$$

$$- \tfrac{1}{4}\left[\frac{1}{r^2} + \frac{m^2\pi^2 \cos^2\dfrac{r\pi}{2a}}{4a^2\left(1 + m \sin\dfrac{r\pi}{2a}\right)^2} + \frac{2m\pi\cos\dfrac{r\pi}{2a}}{2ar\left(1 + m \sin\dfrac{r\pi}{2a}\right)}\right]$$

$$= \frac{(1 - 4s^2)}{4r^2} + k^2 + m\left[-k^2 \sin\frac{r\pi}{2a} + \frac{\pi^2}{8a^2}\sin\frac{r\pi}{2a} - \frac{\pi}{4\,ar}\cdot\cos\frac{r\pi}{2a}\right]$$

$$+ m^2\left[k^2 \sin^2\frac{r\pi}{2a} - \frac{\pi^2}{8a^2}\sin^2\frac{r\pi}{2a} + \frac{\pi}{4\,ar}\sin\frac{r\pi}{2a}\cdot\cos\frac{r\pi}{2a}\right.$$

$$\left. + \frac{\pi^2}{16a^2}\cos^2\left(\frac{r\pi}{2a}\right)\right]$$

where $k^2 = \dfrac{\sigma^2}{gho}$ which is always positive, and as m is small, terms containing m^3 and higher powers of m are neglected.

Now the right side can be put in the form

$$\frac{1 - 4s^2}{4r^2} + k^2 + m\left[\left(\frac{\pi^2}{8a^2} - k^2\right)\sin\frac{r\pi}{2a} - \frac{\pi}{4ar}\cos\frac{r\pi}{2a}\right]$$

$$+ m^2\left[\left(\frac{k^2}{2} - \frac{\pi^2}{32a^2}\right) + \frac{\pi}{8a}\frac{\sin\dfrac{r\pi}{a}}{r} + \left(\frac{3\pi^2}{32a^2} - k^2\right)\cos\frac{r\pi}{a}\right]$$

$$= k^2 + \beta_1 + \frac{1 - 4s^2}{4r^2} + \alpha_1 \sin\frac{r\pi}{2a} + \frac{\alpha_2}{r}\cos\frac{r\pi}{2a} + \frac{\beta_2}{r}\sin\frac{r\pi}{a} + \beta_3 \cos\frac{r\pi}{a}$$

where

$$\alpha_1 = \left(\frac{\pi^2}{8a^2} - k^2\right)m \quad \ldots \ldots \text{ a quantity of the first order of smallness.}$$

$$\alpha_2 = -\frac{m\pi}{4a} \quad \ldots \ldots \ldots \text{ 1st order}$$

$$\beta_1 = m^2 \left(\frac{k^2}{2} - \frac{\pi^2}{32a^2} \right) \quad . \quad . \quad . \quad . \text{ 2nd order of smallness}$$

$$\beta_2 = m^2 \frac{\pi}{8a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \text{ 2nd order}$$

$$\beta_3 = m^2 \left(\frac{3\pi^2}{32a^2} \right) - k^2) \quad . \quad . \text{ 2nd order of smallness.}$$

Thus the equation takes the form

$$\frac{d^2u}{dr^2} + \left(k^2 - \frac{4s^2}{4r^2} \cdot \frac{1}{} \right) u + \left[\alpha_1 \sin \frac{r\pi}{2a} + \alpha_2 \frac{\cos \frac{r\pi}{2a}}{r} \right] u$$

$$+ \left[\beta_1 + \beta_2 \frac{\sin \frac{r\pi}{a}}{r} + \beta_3 \cos \frac{r\pi}{a} \right] u = 0 \qquad . \qquad . \qquad . \quad (3)$$

We shall consider s to be a positive integer throughout unless otherwise stated.

For the first approximation we neglect terms containing the first and second powers of m, that is, we solve the equation

$$\frac{d^2u}{dr^2} + \left(k^2 - \frac{4s^2 - 1}{4r^2} \right) u = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (4)$$

In terms of ζ this was of the form

$$\frac{d^2\zeta}{dr^2} + \frac{1}{r} \frac{d\zeta}{dr} + \left(k^2 - \frac{s^2}{r^2} \right) \zeta = 0$$

Transforming this equation by the relation $kr = p$

we get $\frac{d^2\zeta}{dp^2} + \frac{1}{p} \frac{d\zeta}{dp} + \left(1 - \frac{s^2}{p^2} \right) \zeta = 0$

which is Bessel Equation.

Therefore the solution of (4) is $u = r^{\frac{1}{2}} J_s (kr)$

$$\text{for } \zeta = u e^{-\frac{1}{2} \int \frac{dr}{r}} = u r^{-\frac{1}{2}}$$

We denote this solution by u_0.

$\therefore u_0 = r^{\frac{1}{2}} J_s (kr)$

To get a closer approximation we shall next retain in (3) terms upto the first power of m.

The equation is then

$$\frac{d^2u}{dr^2} + \left(k^2 - \frac{4s^2 - 1}{4r^2} \right) u + \left[\alpha_1 \sin \frac{r\pi}{2a} + \alpha_2 \frac{\cos \frac{r\pi}{2a}}{r} \right] u = 0$$

To solve this put $u = u_0 + u_1$

$$= r^{\frac{1}{2}} J_s (kr) + u_1 \text{ where } u_1 \text{ contains terms of the first}$$

order of smallness.

Then the equation becomes.

$$\frac{d^2 u_1}{dr^2} + \left(k^2 - \frac{4s^2 - 1}{4r^2} \right) u_1 + \left[\alpha_1 \sin\frac{r\pi}{2a} + \alpha_2 \cos\frac{\frac{r\pi}{2a}}{r} \right] r^{\frac{1}{2}} J_s (kr) = 0 \qquad . \qquad . \quad (5)$$

[2] Since the series for $\sin \frac{r\pi}{2a}$, $\cos \frac{r\pi}{2a}$ and $J_s (kr)$ are absolutely convergent for finite values of r, we can multiply the series for sin and cos functions with J_s functions term by term, and the resulting series will be absolutely convergent and their values will be $\sin \frac{r\pi}{2a} . J_s(kr)$ and $\cos \frac{r\pi}{2a} J_s (kr)$ respectively.

On multiplying we get

$$\sin \frac{r\pi}{2a} . J_s (kr) = \sum_{N=0}^{\infty} (-1)^N r^{s+2N+1} \left[\frac{(k/2)^{s+2N} \pi/2a}{\Gamma(s+N+1) \Gamma(N+1) 1!} \right.$$

$$\left. + \frac{(k/2)^{s+2N-2}(\pi/2a)^3}{\Gamma(s+N) \Gamma(N) 3!} \cdots + \frac{(k/2)^s (\pi/2a)^{2N+1}}{\Gamma(s+1)\Gamma(1) \overline{(2N+1)}} \right]$$

$$\cos \frac{r\pi}{2a} . J_s (kr) = \sum_{N=0}^{\infty} (-1)^N r^{s+2N} \left[\frac{(k/2^s+2N}{\Gamma(s+N+1) \Gamma(N+1) 1!} \right.$$

$$\left. + \frac{(k/2)^{s+2N-2}(\pi/2a)^2}{\Gamma(s+N) \Gamma(N) 2!} \cdots + \frac{(k/2)^s (\pi/2a)^{2N}}{\Gamma(s+1) \Gamma(1) 2N!} \right]$$

Thus $- \left[\alpha_1 \sin \frac{r\pi}{2a} + \alpha_2 \frac{\cos \frac{r\pi}{2a}}{r} \right] J_s (kr) . r^{1/2}$ can be put in the form

$$\sum_{N=0}^{\infty} A_{s+2N-\frac{1}{2}} . r^{s+2N-\frac{1}{2}}$$

where $A_{s-\frac{1}{2}} = - \alpha_2 \left[(k/2)^s . \frac{1}{\Gamma(s+1) \Gamma 1} \right]$

$$A_{s+3/2} = - \alpha_1 \left[\frac{(k/2)^s \pi/a}{\Gamma(s+1) \Gamma 1} \right] + \alpha_2 \left[\frac{(k/2)^{s+2} - 1}{\Gamma(s+2) \Gamma(2)} + \frac{(k/2)^s (\pi/2a)^2}{\Gamma(s+1) \Gamma 1 \, 2!} \right]$$

$$A_{s+2N-\frac{1}{2}} = (-1)^N \left[\frac{(k/2)^{s+2N}}{\Gamma(s+N+1)\Gamma(N+1)} + \frac{(k/2)^{s+2N-2}(\pi/2a)^2}{\Gamma(s+N)\Gamma(N) \, 2!} \right.$$

$$\left. \cdots + \frac{(k/2)^s (\pi/2a)^{2N}}{\Gamma(s+1) \Gamma(1) \, 2N!} \right] (-\alpha_2)$$

$$+(-1)^{N-1}\left[\frac{(k/2)^{s+2N-2} \cdot \pi/2a}{\Gamma(s+N)\ \Gamma(N)\ 1!} + \frac{(k/2)^{s+2N-4}\ (\pi/2a)^3}{\Gamma(s+N-1)\ \Gamma(N-1)\ 3!} +\right.$$

$$\left.\cdots + \frac{(k/2)^s\ (\pi/2a)^{2N-1}}{\Gamma(s+1)\ \Gamma(1)\ (2N-1)}\right](-\alpha_1)$$

$$= -\alpha_2\, C_N - \alpha_1\, S_{N-1}$$

where C_N = coeff. in the Nth term in $\cos\dfrac{r\pi}{2a} \cdot J_s\,(kr)$

S_{N-1} = coeff. in the $(N-1)^{th}$ term in $\cos\dfrac{r\pi}{2a} \cdot J_s\,(kr)$

Thus the equation to be solved becomes

$$\frac{d^2 u_1}{dr^2} +(k^2 - \frac{4s^2-1}{4r^2})\, u_1 = \sum_{N=0}^{\infty} r^{s+2N-\frac{1}{2}}\,(-\alpha_2\, C_N - \alpha_1\, S_{N-1}) \quad \cdots \quad (6)$$

To solve this put $u_1 = \displaystyle\sum_{N=0}^{\infty} d_N\,(r/2a)^{s+2N-\frac{1}{2}}$

Substituting this value of u_1 on the left side and equating coeffs. of like powers of r we get the equations giving values of d_N

$$\frac{d_0\, k^2}{(2a)^{s-\frac{1}{2}}} + \frac{d_1}{(2a)^{s+\frac{3}{2}}}\left\{(s+3/2)\ (s+\tfrac{1}{2}) - \frac{4s^2-1}{4}\right\} = -\alpha_2\, C_0$$

$$\frac{d_1\, k^2}{(2a)^{s+\frac{3}{2}}} + \frac{d_2}{(2a)^{s+\frac{7}{2}}}\left\{(s+7/2)\ (s+5/2) - \frac{4s^2-1}{1}\right\} = -\alpha_2\, C_1 - \alpha_1\, S_0$$

$$\frac{d_2\, k^2}{(2a)^{s+\frac{7}{2}}} + \frac{d_3\left\{(s+11/2)\ (s+9/2) - \frac{4s^2-1}{4}\right\}}{(2a)^{s+\frac{7}{2}}} = -\alpha_2\, C_2 - \alpha_1\, S_1$$

$$\frac{d_{N-1}\, k^2}{(2a)^{s+2N-\frac{5}{2}}} + \frac{d_N\left\{(s+2N-\frac{1}{2})\ (s+2N-3/2) - \frac{4s^2-1}{4}\right\}}{(2a)^{s+2N-\frac{1}{2}}} = -\alpha_2 C_{N-1} - \alpha_1 S_{N-2}$$

$$\frac{d_N k^2}{(2a)^{s+2N-\frac{1}{2}}} + \frac{d_{N+1}\left\{(s+2N+3/2)\ (s+2N+1/2) - \frac{4s^2-1}{4}\right\}}{(2a)^{s+2N+3/2}} = -\alpha_2\, C_N - \alpha_1 S_{N-1}$$

Taking d_0 to be an arbitrary constant, the other constants are given by the above equations in terms of d_0, s and k.

We shall next test the convergence of the resulting series

$$u_1 = \sum_{N=0}^{\infty} d_N\ (r/2a)^{s+2N-\frac{1}{2}}$$

From the above equations we get

$$\frac{d_1}{(2a)^{s+3/2}} = \left\{ -\alpha_2\, C_0 - \frac{d_0\, k^2}{(2a)^{s-\frac{1}{2}}} \right\} \quad \frac{1}{\left\{ (s+3/2)\,(s+1/2) - \frac{4s^2-1}{4} \right\}}$$

$$\frac{d_2}{(2a)^{s+7/2}} = \frac{(-\alpha_2\, C_1 - \alpha_1\, S_0)}{\left\{ (s+7/2)\,(s+5/2) - \frac{4s^2-1}{4} \right\}}$$

$$- \frac{k^2 \left\{ -\alpha_2\, C_0 - \frac{d_0\, k^2}{(2a)^{s-\frac{1}{2}}} \right\}}{\left\{ (s+7/2)\,(s+5/2) - \frac{4s^2-1}{4} \right\} \left\{ (s+3/2)\,(s+\frac{1}{2}) - \frac{4s^2-1}{4} \right\}}$$

$$\frac{d_3}{(2a)^{s+11/2}} = \frac{(-\alpha_2\, C_2 - \alpha_1\, S_1}{\left\{ (s+11/2)\,(s+9/2) - \frac{4s^2-1}{4} \right\}}$$

$$- \frac{k^2\,(-\alpha_2\, C_1 - \alpha_1\, S_0)}{\left\{ (s+11/2)\,(s+9/2) - \frac{4s^2-1}{4} \right\} \left\{ (s+\frac{7}{2})\,(s+\frac{5}{2}) - \frac{4s^2-1}{4} \right\}}$$

$$+ \frac{k^4 \left(-\alpha^2\, C_0 - \frac{d_0\, k^2}{(2a)^{s-\frac{1}{2}}} \right)}{\left\{ (s+11/2)\,(s+9/2) - \frac{4s^2-1}{4} \right\} \left\{ (s+7/2)\,(s+5/2) - \frac{4s^2-1}{4} \right\} \left\{ (s+3/2)\,(s+\frac{1}{2}) - \frac{4s^2-1}{4} \right\}}$$

$$\frac{d_N}{(2a)^{s+2N-\frac{1}{2}}} = \frac{(-\alpha_2\, C_{N-1} - \alpha_1\, S_{N-2})}{\left\{ (s+2N-\frac{1}{2})\,(s+2N-3/2) - \frac{4s^2-1}{4} \right\}}$$

$$- \frac{k^2\,(-\alpha_2\, C_{N-2} - \alpha_1\, S_{N-3})}{\left\{ (s+2N-\frac{1}{2})\,(s+2N-3/2) - \frac{4s^2-1}{4} \right\} \left\{ (s+2N-5/2)\,(s+2N-7/2) - \frac{4s^2-1}{5} \right\}}$$

$$+ \cdots + \frac{(-1)^{N-1}\, k^{N-2} \left\{ -\alpha_2\, C_0 - \frac{d_0\, k^2}{(2a)^{s-\frac{1}{2}}} \right\}}{\left\{ (s+2N-\frac{1}{2})\,(s+2N-3/2 - \frac{4s^2-1}{4} \right\} \cdots \left\{ (s+3/2)\,(s+\frac{1}{2}) - \frac{4s^2-1}{4} \right\}} \text{to } N \text{ factors}$$

$$\frac{d_{N+1}}{(2a)^{s+2N+3/2}} = \frac{(-\alpha_2\, C_N - \alpha_1\, S_{N-1})}{\left\{ (s+2N+3/2)\,(s+2N+\frac{1}{2}) - \frac{4s^2-1}{4} \right\}}.$$

$$- \frac{k^2 \left\{ -\alpha_2\, C_{N-1} - \alpha_1\, S_{N-2} \right\}}{\left\{ \ \right\} \left\{ (s+2N-\frac{1}{2})\,(s+2N-3/2) - \frac{4s^2-1}{4} \right\}} +$$

$$+\dots,+\frac{(-1)^N \; k^{2N}\left\{-\alpha_2 C_0-\frac{d_0 \, k^2}{(2a)^{s-\frac{1}{2}}}\right\}}{\left\{(s+2N+3/2)(s+2N+\frac{1}{2})-\frac{4s^2-1}{4}\right\}\cdots\left\{\;\right\}\dots\dots\left\{(s+3/2)(s+\frac{1}{2})-\frac{4s^2-1}{4}\right\}}$$

$$\dots \text{ to } (N+1) \text{ factors.}$$

we may put

$$\frac{d_N}{(2a)^{s+2N-\frac{1}{2}}} \text{ and } \frac{d_{N+1}}{(2a)^{s+2N+3/2}} \text{ in the form } \frac{d_N}{(2a)^{s+2N-\frac{1}{2}}}$$

$$=\frac{(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2})}{\left\{(s+2N-\frac{1}{2})(s+2N-\frac{3}{2})-\frac{4s^2-1}{4}\right\}}$$

$$\left[\;1-\frac{k^2(-\alpha_2 C_{N-2}-\alpha_1 S_{N-3})}{(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2})\left\{(s+2N-5/2)(s+2N-7/2-\frac{4s^2-1}{4}\right\}}\right.$$

$$+\dots\dots+\frac{(-1)^{N-1}k^{2N-2}\left\{\alpha_2 c_0-\frac{d_0 \, k^2}{(2a)^{s-\frac{1}{2}}}\right\}}{(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2})\left\{(s+2N-5/2)(s+2N-7/2-\frac{4s^2-1}{4}\right\}}$$

$$\left.+\dots\dots\left\{(s+3/2)(s+\frac{1}{2})-\frac{4s^2-1}{4}\right\}\right)$$

$$\frac{d_{N+1}}{(2a)^{s+2N+3/2}}$$

$$=\frac{(-\alpha_2 c_N-\alpha_1 S_{N-1})}{\left\{(s+2N+3/2)(s+2N+\frac{1}{2})-\frac{4s^2-1}{4}\right\}}$$

$$\left[\;1-\frac{k^2(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2}}{(-\alpha_2 C_{N-1}-\alpha_1 S_{N-1})\left\{(s+2N-\frac{1}{2})(s+2N-3/2)-\frac{4s^2-1}{4}\right\}}\right.$$

$$+\dots\times\frac{(-1)^N k^{2N}\left\{-\alpha_2 c_0-\frac{d_0 \, k^2}{(2a)^{s-\frac{1}{2}}}\right\}}{\left\{-\alpha_2 c-\alpha_1 S_{N-1}\right\}\left\{(s+2N-\frac{1}{2})(s+2N\;3/2)-\frac{4s^2-1}{4}\right\}}$$

$$\left.\dots\dots\times\left\{(s+3/2)(s+1/2)-\frac{4s^2-1}{7}\right\}\right)$$

It is easy to see that as N tends to infinity, the series within the big brackets in the above tend to the same limit, say D. Then we get

$$\underset{N\to\infty}{\mathrm{Lt}}\;\frac{d_{N+1}}{d}\frac{(r/2a)^{s+2N+3/2}}{(r/2a)^{s+2N-\frac{1}{2}}}=\frac{\mathrm{Lt}\;D(-\alpha_2 C-\alpha_1 S_{N-1}).\,N^2 \, r^2}{D(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2})N^2.\,(2a)^2}$$

$$=\mathrm{Lt}\;\frac{(-\alpha_1 C_N-\alpha_1 S_{N-1})\,r^2}{(-\alpha_2 C_{N-1}-\alpha_1 S_{N-2})(2a)^2}$$

Now $r \leq 2a$ and since C_N and S_N are coefficients in the product $\cos\frac{r\pi}{2a} J_s (kr)$

and $\sin \frac{r\pi}{2a} J_s (kr)$, which are convergent series,

$$c^N < C_{N-1}, \quad S_N < S_{N-1}$$

$$\therefore \; Lt \; \frac{(-a_2 c_N - \alpha_1 S_{N-1}) r/2a)^2}{(-\alpha_2 C_{N-1} - \alpha_1 S_{N-2})} < 1$$

$\therefore$ the series $\qquad u_1 = \sum_{N=0}^{\infty} d \; (r/2a)^{s+2N-\frac{1}{2}}$

is convergent.

Thus the solution of the equation

$$\frac{d^2 u}{dr^2} + \left(k^2 - \frac{4s^2-1}{4r^2} \right) u + \left[\alpha_1 \sin \frac{r\pi}{2a} + \alpha_2 \frac{\cos\frac{r\pi}{2a}}{r} \right] u = 0$$

is given by $u = u_0 + u_1 = r^{\frac{1}{2}} J_s (kr) + \sum_{N=0}^{\infty} d_N (r/2a)^{s+2N-\frac{1}{2}}$

In terms of ζ we have

$$\zeta = u \cdot e^{-\frac{1}{2}\int P dr} \qquad \text{where } P = \frac{1}{r} + \frac{m\pi}{2a} \cdot \frac{\cos\frac{r\pi}{2a}}{(1+m\sin r\pi/2a)}$$

$$\therefore \; e^{-\frac{1}{2}\int P dr} = r^{-\frac{1}{2}} \left(1 + m \sin \frac{r\pi}{2a} \right)^{-\frac{1}{2}}$$

$$\therefore \; \zeta = r^{-\frac{1}{2}} \left(1 + m \sin \frac{r\pi}{22} \right)^{-\frac{1}{2}} \left[r^{\frac{1}{2}} J_s (kr) + \sum_{N=0}^{\infty} d_N (r/2a)^{s+2N-\frac{1}{2}} \right]$$

Therefore the complete solution of the equation

$$\frac{\partial^2 \zeta}{\partial t^2} = g \left\{ \frac{\partial}{\partial x} \left(h \frac{\partial \zeta}{\partial x} \right) + \frac{\partial}{\partial y} \left(h \frac{\partial \zeta}{\partial y} \right) \right\}$$

is $\zeta = e^{i\sigma t} \cos (s\theta) r^{-\frac{1}{2}} (1 + m \sin r\pi/2a)^{-\frac{1}{2}} [r^{\frac{1}{2}} J_s (kr) + \sum_{N=0}^{\infty} d_N (r/2a)^{s+2N-\frac{1}{2}}]$

Permissible values of the frequency are given by applying the boundary

condition $\frac{\partial \zeta}{\partial r} = 0$ at $r = 2a$

It is to be noted that so far we have taken s to be a positive integer. It is found that for values of s such that $2s$ is an odd integer, the first approximate solution u_0 comes out in finite number of terms. But

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even in these cases the next approximation contains infinite number of terms. We shall illustrate the point by considering the solution for some particular values of s. If $2s$ is an odd integer, we can put $2s = 2l + 1$, where l is an integer. Then $\frac{4s^2 - 1}{4} = l(l+1)$

$\therefore$ the equation (3) takes the form $\frac{d^2u}{dr^2} + k^2u = \frac{l(l+1)}{r^2}. u$, where terms of the 1st and 2nd order of smallness are neglected. The [3] solution of this equation is found to be of the form

$$u = r^{l+1} \left(\frac{1}{r} \frac{d}{dr} \right)^{l+1} (A e^{-ikr} + B e^{ikr}) \qquad \text{[cf. Art. 112 Forsyth]}$$

We consider the case $s = \frac{1}{2}$

We then solve the equation

$$\frac{d^2u}{dr^2} + k^2 u = \left[-\alpha_1 \sin \frac{r\pi}{2a} - \alpha_2 \frac{\cos \frac{r\pi}{2a}}{r} \right] u$$

We retain terms only up to the first order of smallness.

The first approximate solution, when the right side is omitted is $u = u_0 = \cos(kr)$

To get the next approximation, substitute $u = u_0 + u_1$ where u_1 contains only first order terms. The equation to be solved is then

$$\frac{d^2u_1}{dr^2} + k^2u_1 = -\left[\alpha_1 \sin \frac{r\pi}{2a} + \alpha_2 \frac{\cos \frac{r\pi}{2a}}{r} \right] u_0$$

$$= -\frac{\alpha_1}{2a} \left[\sin \left(\frac{\pi}{2a} + k \right) r + \sin (\pi/2a - k) r \right]$$

$$- \frac{\alpha_2}{2r} \left[\cos \left(\frac{\pi}{2a} + k \right) r + \cos \left(\frac{\pi}{2a} - k \right) r \right]$$

A particular solution of this equation is

$$u_1 = -\frac{\alpha_1}{2} \frac{\sin \left(\frac{\pi}{2a} + k \right) r}{-\left(\frac{\pi}{2a} + k \right)^2 + k^2} - \frac{\alpha_1}{2} \frac{\sin \left(\frac{\pi}{2a} - k \right) r}{k^2 - \left(\frac{\pi}{2a} - k \right)^2}$$

$$- \frac{\alpha_2}{2} \cos \left(\frac{\pi}{2a} + k \right) r \left\{ \left(D + \frac{\pi}{2a} + k \right)^2 + k^2 \right\}^{-1} \left(\frac{1}{r} \right)$$

$$- \frac{\alpha_2}{2} \cos \left(\frac{\pi}{2a} - k \right) r \left\{ \left(D + \frac{\pi}{2a} - k \right)^2 + k^2 \right\}^{-1} \left(\frac{1}{r} \right)$$

Thus to the first order of smallness, the solution is $u = u_0 + u_1$

$$\therefore \quad \zeta \sqrt{r\left(1 + m \sin \frac{r\pi}{2a}\right)} = e^{i\sigma t} \cos(\theta/2)[u_0 + u_1]$$

which contains infinite number of terms.

We next consider the case $s = 3/2$.

The equation in u becomes

$$\frac{d^2u}{dr^2} + k^2u - \frac{2u}{r^2} = -\left[\alpha_1 \sin \frac{r\pi}{2a} + \frac{\alpha_2}{r} \cos \frac{r\pi}{2a}\right] u.$$

The solution of $\dfrac{d^2u}{dr^2} + k^2u - \dfrac{2u}{r^2} = 0$ is found to be $u_0 = \sin(kr) + \dfrac{\cos(kr)}{r}$

To get the next approximation put $u = u_0 + u_1$ in the original equation and we get

$$\frac{d^2u_1}{dr^2} + \left(k^2 - \frac{2}{r^2}\right)u_1 = -\left[\alpha_1 \sin \frac{r\pi}{2a} + \frac{\alpha_2}{r} \cos \frac{r\pi}{2a}\right] \cdot \left[\sin(kr) + \frac{\cos(kr)}{r}\right]$$

$$= -\tfrac{1}{2}\left[\frac{\alpha_1 + \alpha_2}{r} \sin\left(k + \frac{\pi}{2a}\right)r + \frac{\alpha_2 - \alpha_1}{r} \sin\left(k - \frac{\pi}{2a}\right)r\right.$$

$$\left. + \left(\frac{\alpha_2}{r^2} - \alpha_1\right)\cos\left(k + \frac{\pi}{2a}\right)r + \left(\alpha_1 + \frac{\alpha_2}{r^2}\right)\cos\left(k - \frac{\pi}{2a}\right)r\right]$$

The right side can be expanded in a power series in r and a series solution of the equation can be obtained.

On expanding the right side becomes

$$-\tfrac{1}{2}\left\{\alpha_1 \frac{\pi}{a} + 2\alpha_2 k - \alpha_2\left(k^2 + \frac{\pi^2}{4a^2}\right)\right\} - \frac{\alpha_2}{r^2}$$

$$+ \frac{r^2}{2}\left\{(\alpha_1 + \alpha_2)\frac{\left(k + \frac{\pi}{2a}\right)^3}{\underline{|3}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2a}\right)^3}{\underline{|3}} - \frac{k\pi\alpha_1}{a}\right.$$

$$\left. - \frac{\left(k + \frac{\pi}{2a}\right)^4 + \left(k - \frac{\pi}{2a}\right)^4}{\underline{|4}}\cdot\alpha_2\right\}$$

$$- \frac{r^4}{2}\cdot\left\{(\alpha_1 + \alpha_2)\frac{\left(k + \frac{\pi}{2a}\right)^5}{\underline{|5}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2a}\right)^5}{\underline{|5}}\right.$$

$$\left. \frac{\alpha_1\left(k - \frac{\pi}{2a}\right)^4}{\underline{|4}} - \frac{\left(k + \frac{\pi}{2a}\right)^4}{\underline{|4}}\alpha_1 - \frac{\left(k + \frac{\pi}{2a}\right)^6 + \left(k - \frac{\pi}{2a}\right)^6}{\underline{|6}}\cdot\alpha_2\right\}$$

$+ \ldots\ldots$

$$+ (-1)^{n+2} \frac{r^{2n-2}}{2} \left[(a_1 + a_2) \frac{\left(k + \frac{\pi}{2a}\right)^{2n-1}}{\underline{|2n-1}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2}\right)^{2n-1}}{\underline{|2n-1}} \right.$$

$$+ a_1 \frac{\left(k - \frac{\pi}{2a}\right)^{2n-2} - \left(k + \frac{\pi}{2a}\right)^{2n-2}}{\underline{|2n-2}} +$$

$$\left. (-1)^n . a_2 \frac{\left(k + \frac{\pi}{2a}\right)^{2n} + \left(k - \frac{\pi}{2a}\right)^{2n}}{\underline{|2n}} \right]$$

$+ \ldots\ldots$

$$= \frac{1}{2} \sum_{n=0}^{\infty} (-1)^{n+2} \frac{r^{2n-2}}{1} \left[(a_1 + a_2) \frac{\left(k + \frac{\pi}{2a}\right)^{2n-1}}{\underline{|2n-1}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2a}\right)^{2n-1}}{\underline{|2n-1}} \right.$$

$$\left. + a_1 \frac{\left(k - \frac{\pi}{2a}\right)^{2n-2} - \left(k + \frac{\pi}{2a}\right)^{2n-2}}{\underline{|2n-2}} + (-1)^n . a_2 \frac{\left(k + \frac{\pi}{2a}\right)^{2n} + \left(k - \frac{\pi}{2a}\right)^{2n}}{\underline{|2n}} \right]$$

To solve the equation put $u_1 = \sum_{n=0}^{\infty} p_{2n} r^{2n}$ on the left side. Equating coefficient of like powers of r, p^s are given by the following equations

$$p_0 k^2 - 2p_2 + 2p_2 = -\tfrac{1}{2} \left\{ \alpha_1 \frac{\pi}{a} + 2 \alpha_2 k - a_2 \left(k^2 + \frac{\pi^2}{4a^2} \right) \right\}$$

$$- 2 p_0 = - \alpha_2$$

$$10 p_4 + k^2 p_2 = \tfrac{1}{2} \left\{ \frac{(a_1 + a_2)\left(k + \frac{\pi}{2a}\right)^3}{\underline{|3}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2a}\right)^3}{\underline{|3}} - \frac{k\pi}{a} \right.$$

$$\left. - \frac{\left(k + \frac{\pi}{2a}\right)^4 + \left(k - \frac{\pi}{2a}\right)^4}{\underline{|4}} \right\}$$

$$28 p_6 + k^2 p_6 = - \tfrac{1}{2} \left\{ \frac{(a_1 + a_2)\left(k + \frac{\pi}{2a}\right)^5}{\underline{|5}} + \frac{(\alpha_2 - \alpha_1)\left(k - \frac{\pi}{2a}\right)^5}{\underline{|5}} \right.$$

$$\left. + \frac{\left(k - \frac{\pi}{2a}\right)^4 - \left(k + \frac{\pi}{2a}\right)^4}{\underline{|4}} - \frac{\left(k + \frac{\pi}{2a}\right)^6 + \left(k - \frac{\pi}{2a}\right)^6}{\underline{|6}} \right\}$$

$$\{2n(2n-1)-2\}\cdot p_{2n}+k^2\,p_{2n-2}=\tfrac{1}{2}\,(-1)^{n+2}\left[\dfrac{(\alpha_1+\alpha_2)\left(k+\dfrac{\pi}{2a}\right)^{3n-1}}{\underline{|2n-1}}+\right.$$

$$\dfrac{(\alpha_2-\alpha_1)\left(k-\dfrac{\pi}{2a}\right)^{2n-1}}{\underline{|2n-1}}+\alpha_1\dfrac{\left(k-\dfrac{\pi}{2a}\right)^{2n-2}-\left(k+\dfrac{\pi}{2a}\right)^{2n-2}}{\underline{|2n-2}}\cdot$$

$$+(-1)^n\cdot\alpha_2\dfrac{\left(k+\dfrac{\pi}{2a}\right)^{2n}+\left(k-\dfrac{\pi}{2a}\right)^{2n}}{\underline{|2n}}\left.\right]$$

The first two equations give an interdependence between α_1 and α_2. The remaining equations determine values of p_4, p_6 etc. in terms of p_2 which comes out to be arbitrary but can be evaluated later on by applying the boundary condition as shown later on.

Thus the complete solution is $u=u_0+u_1$

$$=\zeta\sqrt{\left(1+m\sin\dfrac{r\pi}{2a}\right)}\cdot r$$

$$\therefore\ \zeta\sqrt{\left(1+m\sin\dfrac{r\pi}{2a}\right)}r=e^{i\sigma t}\cos\left(\dfrac{3\theta}{2}\right)\left[\sin(kr)+\dfrac{\cos(kr)}{r}+\sum_{n=0}^{\infty}p_{2n}\cdot r^{2n}\right]$$

The boundary condition $\dfrac{\partial\zeta}{\partial r}=0$ at $r=2a$ may be used to find suitable values of p_2.

The interdependence between α_1 and α_2 reduces to

$$\alpha_1\ \dfrac{\pi}{2a}=\alpha_2\left(\dfrac{\pi^2}{8a^2}-k\right)\qquad\text{substituting the values of }\alpha_1\text{ and }\alpha_2$$

we get $\ k^2+k/2-\dfrac{3\pi^2}{16a^2}=0$

or $\qquad k=\dfrac{-1\pm\sqrt{1+\dfrac{3\pi^2}{a^2}}}{4}$ where $k^2=\dfrac{\sigma^2}{gb_0}$

This gives admissible values for σ.

Thus we have seen that for values of s such that $2s$ is an odd integer, the 2nd approximate solution of the equation involves infinite number of terms.

We shall next consider the case when the basin is rotated about its vertical axis with constant velocity ω.

Let the axis of the basin be taken to be the z axis and the origin be taken in the undisturbed free surface before rotation ensues. The axes of x and y are now supposed to rotate in their own plane with

the prescribed angular velocity w, let us denote by, u, v and w the velocities at time t, relative to these axes, of the particle which then occupies the position (x, y, z). The actual velocities of the same particle, parallel to the instantaneous positions of the axes, will be $u - wy$, $v + wx$, w and the accelerations in the same directions will be

$$\frac{Du}{Dt} - 2\,w\,v - w^2 x, \quad \frac{Dv}{Dt} + 2\,w\,u - w^2 y, \quad \frac{Dw}{Dt}.$$

We shall assume the relative motion to be infinitely small, so that we may replace $\frac{D}{Dt}$ by $\frac{\partial}{\partial t}$.

Now let z_0 be the ordinate of the free surface when there is relative equilibrium under gravity alone, so that

$$z_0 = \tfrac{1}{2}\frac{w^2}{g}(x^2 + y^2) + \text{const.} \quad . \qquad . \quad . \qquad . \qquad . \qquad . \quad (1)$$

For simplicity we will suppose that the slope of this surface is everywhere small, in other words, if r be the greatest distance of any part of the sheet from the axis of rotation, $\dfrac{w^2 r}{g}$ is assumed to be small.

Let $z_0 + \zeta$ denote the ordinate of the free surface when disturbed, then on the usual assumption that the vertical acceleration of water is small compared with g the pressure at any point (x, y, z) is given by

$$p - p_0 = g\varrho\,(z_0 + \zeta - z) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (2)$$

whence $\quad -\dfrac{1}{\varrho}\dfrac{\partial p}{\partial x} = -w^2 x - g\dfrac{\partial \zeta}{\partial x}$

$$-\dfrac{1}{\varrho}\dfrac{\partial p}{\partial y} = -w^2 y - g\dfrac{\partial \zeta}{\partial y}.$$

The equations of horizontal motion are therefore

$$\frac{\partial u}{\partial t} - 2\,w.\,v = -g\frac{\partial \zeta}{\partial x}, \quad \frac{\partial v}{\partial t} + 2\,w\,u = -g\frac{\partial \zeta}{\partial y} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (3)$$

The equation of continuity is as usual

$$\frac{\partial \zeta}{\partial t} = -\frac{\partial}{\partial x}(hu) - \frac{\partial}{\partial y}(hv),$$

where h denotes the depth from the free surface to the bottom, in the undisturbed condition.

In the case of simple harmonic disturbance the time factor being $e^{i\sigma t}$, the equation (3) and (4) become

$$i\sigma\, u - 2\,wv = -\,g\,\frac{\partial}{\partial x}\,(\zeta)\;,\; i\sigma v + 2\,w\,u = -\,g\,\frac{\partial\zeta}{\partial y} \qquad . \qquad . \qquad . \qquad . \quad (5)$$

and $i\sigma\zeta = -\dfrac{\partial(hu)}{\partial x} - \dfrac{\partial}{\partial y}\,(hv)$ $\qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (6)$

From (5) we find

$$
\left.
\begin{aligned}
u &= \frac{g}{\sigma^2 - 4w^2}\left(i\sigma\,\frac{\partial}{\partial x} + 2w\,\frac{\partial}{\partial y}\right)\zeta \\
v &= \frac{g}{\sigma^2 - w^2}\left(i\sigma\,\frac{\partial}{\partial y} - 2w\,\frac{\partial}{\partial x}\right)\zeta
\end{aligned}
\right\}
\qquad . \qquad . \qquad . \qquad . \qquad . \quad (7)
$$

Introducing polar coordinates (r, θ) and employing the symbols ξ, η to denote displacements along and perpendicular to the radius vector, then since

$\dot{\xi} = i\sigma\xi, \dot{\eta} = i\sigma\eta$ the equations (7) become

$$
\left.
\begin{aligned}
\xi &= \frac{g}{\sigma^2 - 4w^2}\left(\frac{\partial}{\partial r} - \frac{2iw}{\sigma}\cdot\frac{\partial}{r\partial\theta}\right)\zeta \\
\eta &= \frac{ig}{\sigma^2 - 4w^2}\left(\frac{2w}{\sigma}\,\frac{\partial}{\partial r} - i\,\frac{\partial}{r\partial\theta}\right)\zeta
\end{aligned}
\right\}
\qquad . \qquad . \qquad . \qquad . \quad (8)
$$

and equation (4) becomes

$$\zeta = -\frac{\partial}{r\partial r}\,(h\,\xi\,r) - \frac{\partial}{r\partial\theta}\,(h\eta)\,. \qquad . \qquad . \qquad . \qquad . \qquad . \quad (9)$$

Elimination of ξ, η between (8) and (9) gives an equation in ζ alone. We get

$$h\,\frac{\partial^2\zeta}{\partial r^2} + \frac{h}{r^2}\,\frac{\partial^2\zeta}{\partial\theta^2} + \left(\frac{2iwh}{\sigma r} - \frac{2iwh}{\sigma r}\right)\frac{\partial^2\zeta}{\partial r\partial\theta}$$

$$+ \left\{\frac{dh}{dr} + \frac{h}{r} + \frac{2iw}{\sigma r}\cdot\frac{\partial h}{\partial\theta}\right\}\frac{\partial\zeta}{\partial r} + \left\{\frac{1}{r^2}\frac{\partial h}{\partial\theta} + \frac{2iwh}{\sigma r^2} - \frac{2iwh}{\sigma r^2} - \frac{2iw}{\sigma r}\cdot\frac{dh}{dr}\right\}\cdot\frac{\partial\zeta}{\partial\theta}$$

$$+ \frac{\sigma^2 - 4w^2}{g}\cdot\zeta = 0$$

or $\qquad h\,\dfrac{\partial^2\zeta}{\partial r^2} + \dfrac{h}{r^2}\,\dfrac{\partial^2\zeta}{\partial\theta^2} + \left\{\dfrac{dh}{dr} + \dfrac{h}{r} + \dfrac{2iw}{\sigma r}\dfrac{\partial h}{\partial\theta}\right\}\cdot\dfrac{\partial\zeta}{\partial r}$

$$+ \left\{\frac{1}{r^2}\cdot\frac{\partial h}{\partial\theta} - \frac{2iw}{\sigma r}\cdot\frac{dh}{dr}\right\}\frac{\partial\zeta}{\partial\theta} + \frac{\sigma^2 - 4w^2}{g}\,\zeta = 0$$

If we assume that h varies according to the same law as in the first part of the paper, then h is a function of r only and the above equation reduces to

$$h\frac{d^2\zeta}{dr^2} + \frac{h}{r^2}\cdot\frac{\partial^2\zeta}{\partial\theta^2} + \left\{\frac{dh}{dr} + \frac{h}{r}\right\}\frac{\partial\zeta}{\partial r} - \frac{2iw}{\sigma r}\cdot\frac{dh}{dr}\cdot\frac{\partial\zeta}{\partial\theta}\cdot + \frac{\sigma^2 - 4w^2}{g}\cdot\zeta = 0$$

Taking ζ to vary as $e^{i\theta s}$ where s is integral, the equation simplifies to

$$h\left\{\frac{\partial^2\zeta}{\partial r^2} + \frac{1}{r}\frac{\partial\zeta}{\partial r} - \frac{s^2\zeta}{r^2}\right\} + \frac{dh}{dr}\cdot\frac{\partial\zeta}{\partial r} + \left\{\frac{\sigma^2 - 4w^2}{g} + \frac{2sw}{\sigma r}\cdot\frac{dh}{dr}\right\}\cdot\zeta = 0$$

when $h = h_0\left(1 + m\sin\frac{r\pi}{2a}\right)$, the above becomes

$$\frac{\partial^2\zeta}{\partial r^2} + P\frac{\partial\zeta}{\partial r} + Q\zeta = 0 \text{ where}$$

$$P = \frac{1}{r} + \frac{m\pi}{2a}\cdot\frac{\cos\frac{r\pi}{2a}}{\left(1 + m\sin\frac{r\pi}{2a}\right)}$$

$$Q = \frac{\sigma^2 - 4w^2}{gh_0\left(1 + m\sin\frac{r\pi}{2a}\right)} - \frac{s^2}{r^2} + \frac{2sw}{\sigma}\cdot\frac{m\pi}{2a}\cdot\frac{\cos\frac{r\pi}{2a}}{r}$$

It is to be noted that the value of P is the same as in the first part of the problem. As regards Q there is an additional term

$\frac{2sw}{\sigma}\cdot\frac{m\pi}{2a}\cdot\frac{\cos\frac{r\pi}{2a}}{r}$ and instead of k^2 ie $\frac{\sigma^2}{gh_0}$ we now have $\frac{\sigma^2 - 4w^2}{gh_0}$. Hence proceeding as in the first part, we have after transforming the equation in ζ to u by the relation $\zeta = u e^{-\frac{1}{2}\int P dr}$

$$\frac{d^2u}{dr^2} + \left(k_1^2 - \frac{4s^2 - 1}{4r^2}\right)u + \left[\alpha_1\sin\frac{r\pi}{2a} + \alpha_2^1\cos\frac{r\pi}{2a}\right]u$$

$$+ \left[\beta_1 + \beta_2\frac{\sin\frac{r\pi}{2a}}{r} + \beta_3\cos\frac{r\pi}{2a}\right]u = 0$$

where $k_1^2 = \frac{\sigma^2 - 4w^2}{gh_0}$

$$\alpha_2^1 = \alpha_2 + \frac{2sw\pi}{2a\sigma}\cdot m$$

and α_1, α_2, β_1, β_2 and β_3 have the same values as in the first part.

Thus the equation remains essentially similar and with the new notation has the same solution as in the first part. The only difference is in the boundary condition, it being

$$\left(r \; \frac{\partial}{\partial r} - \frac{2iw}{\sigma} \; , \; \frac{\partial}{c\theta} \right) \zeta = 0 \text{ at } r = 2a$$

I express my thanks to Prof. A. C. Banerji under whose guidance the paper was prepared.

References

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[2] Barnard and Child, *Higher Algebra*　　　p ... 335
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EFFECT OF TEMPERATURE OVER VISCOSITY AND ELECTRICAL CONDUCTIVITY OF COLLOIDS OF IRON SILICATES

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Abstract

Colloids of iron silicate were prepared and the viscosity of the different samples (taken at different stages of dialysis) and at different concentrations were measured using special viscometer and arrangement, at different shearing stresses causing the flow. The measurements were done at 30°C, 50°C, and 70°C and also again at 30°C, after keeping the samples at 70°C for half an hour. The specific conductivity was also noted of each sample at the temperatures at which the viscosity measurements were done.

Viscosity was seen to rise with temperature for pure and concentrated samples while a decrease was seen for dilute ones. The impure sample showed the same viscosity after cooling from higher temperatures while pure samples showed a permanent increment in the value. The electrical conductivity was seen to rise in all cases with warming and the value was not repeatable by cooling. The behaviour is explained on the basis of the structure formation of colloid particles and their loss of adsorptive capacity at higher temperatures.

In a previous publication (1) we have reported the preparation of positively charged iron silicate colloid and have studied its behaviour with reference to its viscosity at various stages of purity and concentration. There it was found to yield gels after sufficient purity was attained, and structural flow had also been recognised in the viscosity data when the measurements were carried on different shearing stresses causing the flow in the viscometer.

In preliminary experiments it was seen that the viscosity of the sol of iron silicate increased when the sol was warmed specially when it was pure and concentrated. Ghosh and Banerji (2) have studied the effect of temperature on the viscosity of ferric phosphate sol and have correlated the result with its ageing effect. In this paper we have studied the effect of the temperature over viscosity and specific conductivity of colloids of iron silicates as it has been seen that the sol sets to a gel form when sufficiently pure on warming.

EXPERIMENTAL

Three colloids namely Sol A, Sol B, and Sol C of iron silicates were prepared by the interaction of ferric chloride and sodium silicate solutions as published earlier in a communication from this laboratory (loc. cit.). Sodium silicate solutions of different Na_2O/SiO_2 ratio were used for the preparation of the sols of different compositions by addition of hydrochloric acid or caustic soda solutions in calculated amounts.

The experimental results described here deal with three samples of each iron silicate colloid taken at various stages of purity showing no coagulation, precipitation and gel formation when treated with electrolyte solutions, and are marked as Sol AI, Sol AII, Sol AIII etc. The viscosity relative to water have been measured at three concentrations of each sample viz. Sol AI—without dilution, Sol AI/3—thrice dilution, and Sol AI/6—six times dilution with water, at three different shearing stresses causing the flow, namely, 15 cms., 30 cms, and 60 cms. of the water column and at temperatures 30°C, 50°C, and 70°C. The measurements have also been repeated at 30°C after keeping the sol at 70°C for 30 minutes. The viscosities were measured using a special type of viscometer with the use of a combination of Farrow's and Hosking's methods of viscosity measurements with modification first described by Ghosh and Ayub (3) and also described in detail in the previous communication (loc. cit.).

The electrical conductivity has been measured at the dilutions and temperatures at which the viscosity measurements have been done.

Fe_2O_3 and SiO_2 and chloride contents of each sample taken out of the dialysis bag are also given.

Sol AI—Sample taken before dialysis.

Composition : Fe_2O_3—0.01531 gm. moles per litre.

SiO_2—0.04995 gm. moles per litre.

Cl —0.1356 gm. atoms per litre.

Iron silicate, therefore contains Fe_2O_3 and SiO_2 in the ratio of 1 : 3·26.

The sample did not show coagulation within convenient time with N/10 potassium sulphate solution.

Rates of flow (η_s/η_w)

Temperature	Sol AI			Sol AI/3			Sol AI/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.021	1.021	1.021	1.020	1.020	1.019	1.018	1.018	1.018
50°C	1.039	1.038	1.038	1.016	1.016	1.016	1.010	1.010	1.010
70°C	1.024	1.023	1.023	1.008	1.007	1.007	1.003	1.003	1.003
The sol was cooled back to 30°C	1.021	1.021	1.021	1.020	1.020	1.019	1.018	1.018	1.018

Conductivity in inverse ohms.

Temperature	Sol AI	Sol AI/3	Sol AI/6
30°C	$1 \cdot 321 \times 10^{-2}$	$5 \cdot 1415 \times 10^{-3}$	$2 \cdot 0778 \times 10^{-3}$
50°C	$1 \cdot 814 \times 10^{-2}$	$7 \cdot 224 \times 10^{-3}$	$3 \cdot 685 \times 10^{-3}$
70°C	$2 \cdot 439 \times 10^{-2}$	$9 \cdot 6290 \times 10^{-3}$	$5 \cdot 123 \times 10^{-3}$
The sol was cooled back to 30°C	$1 \cdot 409 \times 10^{-2}$	$5 \cdot 667 \times 10^{-3}$	$2 \cdot 987 \times 10^{-3}$

Sol AII—Sample after 50 hours dialysis.

Composition :

$Fe_2 O_3$—0.01235 gm. moles per litre

SiO_2—0.04662 gm. moles per litre

Cl—0.03390 gm. moles per litre

therefore it contained $Fe_2 O_3$ and SiO_2 in the ratio of 1:3.726.

Rates of flow (η_s/η_w)

Temperature	Sol AII			Sol AII/3			Sol AII/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.028	1.027	1.027	1.024	1.023	1.023	1.015	1.014	1.013
50°C	1.047	1.047	1.047	1.026	1.025	1.021	1.001	1.000	1.000
70°C	1.060	1.059	1.059	1.020	1.020	1.017	1.007	1.005	1.004
The sol was cooled back to 30°C	1.028	1.027	1.027	1.024	1.023	1.023	1.015	1.014	1.013

Conductivity in inverse ohms.

Temperature	Sol AII	Sol AII/3	Sol AII/6
30°C	$1 \cdot 388 \times 10^{-3}$	$5 \cdot 295 \times 10^{-4}$	$2 \cdot 948 \times 10^{-4}$
50°C	$2 \cdot 311 \times 10^{-3}$	$7 \cdot 504 \times 10^{-4}$	$4 \cdot 374 \times 10^{-4}$
70°C	$2 \cdot 801 \times 10^{-3}$	9.979×10^{-4}	$5 \cdot 444 \times 10^{-4}$
The sol was cooled back to 30°C	$1 \cdot 502 \times 10^{-3}$	$5 \cdot 690 \times 10^{-4}$	$3 \cdot 19 \times 10^{-4}$

Sol A III—After 192 hours of dialysis

Composition :

Fe_2O_3—0.01135 gm. moles per litre.

SiO_2—0.04310 gm. moles per litre.

Cl—0.0339 gm. atoms per litre.

Therefore it contained Fe_2O_3 and SiO_2 in the ratio 1:3.797.

The sample was seen to yield gels on suitable coagulation

Rates of flow (η_s/η_w)

Temperature	Sol A III			Sol A III/3			Sol A III/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.702	1.577	1.476	1.190	1.130	1.125	1.092	1.089	1.087
50°C	2.945	2.261	2.112	..	1.409	1.260	1.140	1.087	1.087
70°C	The sol sets to a firm gel form in the viscometer when kept at 70°C within 30 minutes.			Gel formation in the viscometer			Irregular flow due to the precipitation.		

Conductivity in inverse ohms.

Temperature	Sol AIII	Sol AIII/3	Sol AII /6
30°C	$1 \cdot 118 \times 10^{-4}$	$4 \cdot 481 \times 10^{5}$	$2 \cdot 616 \times 10^{-5}$
50°C	$1 \cdot 568 \times 10^{-4}$	$7 \cdot 818 \times 10^{-5}$	$3 \cdot 92 \times 10^{-5}$
70°C	$2 \cdot 194 \times 10^{-4}$	$1 \cdot 397 \times 10^{-4}$	$9 \cdot 32 \times 10^{-5}$
The sol was cooled back to 30°C	$1 \cdot 116 \times 10^{4}$	$6 \cdot 448 \times 10^{-5}$	$5 \cdot 25 \times 16^{-5}$

Sol BI—Before keeping for dialysis, The sample did not coagulate with electrolyte solutions.

Composition :

Fe_2O_3—0.01390 gm. moles per litre.

SiO_2—0.06526 gm. moles per litre.

Cl—0.12080 gm. atoms per litre.

Thus it contained Fe_2O_3 : SiO_2 in the ratio of 1:4.695

Rates of flow (η_s/η_w)

Temperature	Sol BI			Sol BI/3			Sol BI/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.024	1.024	1.024	1.021	1.021	1.020	1.008	1.008	1.007
50°C	1.051	1.050	1.047	1.020	1.016	1.016	1.004	1.004	1.003
70°C	1.072	1.062	1.055	1.021	1.020	1.016	1.007	1.003	1.003
The sol was cooled back to 30°C	1.024	1.024	1.024	1.021	1.021	1.020	1.008	1.008	1.007

Sol BI—

Conductivity in inverse ohms.

Temperature	Sol BI	Sol BI/3	Sol BI/6
30°C	1.0264×10^{-2}	4.80×10^{-3}	2.662×10^{-3}
50°C	1.792×10^{-2}	6.81×10^{-3}	3.710×10^{-3}
70°C	2.269×10^{-2}	9.324×10^{-3}	5.515×10^{-3}
The sol was cooled back to 30°C	1.306×10^{-2}	5.014×10^{-3}	2.900×10^{-3}

Sol BII—After 72 hours dialysis. The sample showed coagulation with electrolytes.

Composition :

Fe_2O_3—0.01050 gm. moles per litre.

SiO_2—0.06327 gm. moles per litre.

Cl—0.024828 gm. atoms per litre.

Therefore it contained Fe_2O_3 and SiO_2 in the ratio of 1:6.026

Rates of flow (η_s/η_w)

Temperature	Sol BII			Sol BII/3			Sol BII/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.042	1.041	1.038	1.021	1.021	1.020	1.006	1.006	1.006
50°C	1.048	1.047	1.047	1.003	1.003	1.002	1.020	1.016	1.016
70°C	1.097	1.095	1.095	1.039	1.037	1.037	1.030	1.030	1.030
The sol was cooled back to 30°C	1.042	1.041	1.038	1.021	1.021	1.020	1.006	1.006	1.006

Conductivity in inverse ohms.

Sol BII—	Sol BII	Sol BII/3	Sol BII/6
30°C	8.863×10^{-4}	3.550×10^{-4}	2.025×10^{-4}
50°C	1.250×10^{-3}	5.933×10^{-4}	2.909×10^{-4}
70°C	1.948×10^{-3}	9.532×10^{-4}	4.429×10^{-4}
The sol was cooled back to 30°C	9.024×10^{-4}	3.972×10^{-4}	2.514×10^{-4}

Sol BIII—After 8 days dialysis. The sol yielded gels with electrolytes on coagulation

Composition :

Fe_2O_3—0.007889 gm. moles per litre.

SiO_2—0.06300 gm. moles per litre.

Cl—0.024828 gm. atoms per litre.

Therefore it contained Fe_2O_3 and SiO_2 in the ratio 1:7.98.

Rates of flow (η_s/η_w)

Temperature	Sol BIII			Sol BIII/3			Sol BIII/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	2.906	2.495	2.262	1.408	1.319	1.265	1.147	1.046	1.145
50°C	Gel set in 30 minutes.			..	7.406	2.642	1.542	1.365	1.230
70°C				Gel set in 30 minutes.			Irregular flow due to precipitation.		

Electrical conductivity in inverse ohms.

Temperature	Sol BIII	Sol BIII/3	Sol BIII/6
30°C	8.015×10^{-5}	3.905×10^{-5}	2.416×10^{-5}
50°C	1.198×10^{-4}	5.946×10^{-5}	3.879×10^{-5}
70°C	1.751×10^{-4}	9.221×10^{-5}	5.192×10^{-5}
The sol was cooled back to 30°C	9.441×10^{-5}	5.266×10^{-5}	3.281×10^{-5}

Sol CI—before dialysis

The sol did not coagulate with electrolyte solutions.

Composition :

Fe_2O_3—0.012456 gm. moles per litre.

SiO_2—0.10652 gm. moles per litre.

Cl—0.11722 gm. atoms per litre.

Therefore it contained Fe_2O_3 and SiO_2 in the ratio of 1:8.545

Rates of flow (η_s/η_w)

Temperature	Sol CI			Sol CI/3			Sol CI/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.078	1.078	1.075	1.050	1.044	1.033	1.024	1.023	1.020
50°C	1.113	1.113	1.112	1.036	1.035	1.033	1.009	1.007	1.007
70°C	1.255	1.253	1.251	1.247	1.247	1.245	1.096	1.095	1.094
The sol was cooled back to 30° C	1.078	1.078	1.075	1.050	1.044	1.033	1.024	1.023	1.020

Conductivity in inverse ohms.

Temperature	Sol CI	Sol CI/3	Sol CI/6
30°C	1.284×10^{-2}	4.699×10^{-3}	2.412×10^{-3}
50°C	1.760×10^{-2}	6.305×10^{-3}	3.467×10^{-3}
70°C	2.346×10^{-2}	9.458×10^{-3}	4.444×10^{-3}
The sol was cooled back to 30°C	1.301×10^{-2}	4.732×10^{-3}	2.501×10^{-3}

Sol CII—Sample taken after 11 days dialysis.

The Sol was seen to coagulate with electrolytes.

Composition :

　　　Fe_2O_3—0.01084 gm. moles per litre.

　　　SiO_2—0.09656 gm. moles per litre.

　　　CI –0.01724 gm. moles per litre.

Therefore it contained Fe_2O_3 and SiO_2 in the ratio of 1:8.906

Rates of flow (η_s/η_w)

Temperature	Sol CII			Sol CII/3			Sol CII/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	1.740	1.738	1.730	1.227	1.227	1.221	1.097	1.096	1.092
50°C	1.669	1.669	1.668	1.214	1.214	1.213	1.096	1.096	1.094
70°C	1.672	1.625	1.624	1.250	1.248	1.244	1.153	1.151	1.150
The sol was cooled back to 30°C	1.740	1.738	1.730	1.227	1.227	1.221	1.097	1.096	1.092

Conductivity in inverse ohms

Temperature	Sol CII	Sol CII/3	Sol CII/6
30°C	6.210×10^{-5}	2.382×10^{-5}	1.491×10^{-5}
50°C	1.134×10^{-4}	4.099×10^{-5}	3.624×10^{-5}
70°C	1.781×10^{-4}	6.619×10^{-5}	4.508×10^{-5}

The sol was cooled
back to 30°C $\qquad$ 9.301 × 10⁻⁴ $\qquad$ 5.008 × 10⁻⁵ $\qquad$ 2.489 × 10⁻⁵

Sol. CIII—Sample taken after 20 days dialysis.

The sol yielded gels on suitable coagulation.

Composition :

Fe₂O₃—0.00674 gm. moles per litre.

SiO₂—0.06612 gm. moles per litre.

Cl —0.01724 gm. atoms per litre.

Therefore it contained Fe₂O₃ and SiO₂ in the ratio of 1:9.809

Rates of flow (η_s/η_w)

Temperature	Sol CIII			Sol CIII/3			Sol CIII/6		
	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.	15 cms.	30 cms.	60 cms.
30°C	2.173	1.874	1.742	1.369	1.268	1.212	1.109	1.109	1.092
50°C	2.035	1.770	1.682	1.332	1.273	1.271	1.092	1.092	1.092
70°C	1.774	1.666	1.612	1.539	1.485	1.442	1.153	1.153	1.150
The sol was cooled back to 30°C	3.42	2.428	1.507	1.276	1.212	1.111	1.109	1.109	1.092

Conductivity in inverse ohms.

Temperature	Sol CIII	Sol CIII/3	Sol CIII/6
30°C	4.161 × 10⁻⁵	1.174 × 10⁻⁵	7.392 × 10⁻⁶
50°C	5.170 × 10⁻⁵	1.844 × 10⁻⁵	1.194 × 10⁻⁵
70°C	8.919 × 10⁻⁵	3.357 × 10⁻⁵	2.568 × 10⁻⁵
The sol was cooled back to 30°C	5.741 × 10⁻⁵	2.159 × 10⁵	1.190 × 10⁻⁵

A perusal of the viscosity and electrical conductivity results reveals that warming of the sol leads to an increase in viscosity in cases of concentrated sols, while the reverse is true for the dilute samples, as a decrease is observed there. The conductivity is seen to increase in all cases with the rise of temperature, the rise is seen to be much more than what can be computed from the change of mobility of the ions of the electrolytic impurities present in the sol at high temperatures. This is more marked in the case of dilute samples. When the temperature is brought back again to 30°C after heating upto 70°C, it is seen that the viscosity values return practically, to their original values, in other words, the viscosity effect is reversible in case of impure samples, while in case of electrical conductivity the increase observed by heating is more or less permanent.

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Considering the above effects with purity it is to be noted that with purer sols. (sol AIII, B III, and C III) the viscosity effects are similar with rise in temperature. The changes in electrical conductivity are also prominent than those observed in the case of impure sols. Purer samples show also an increase in the structural flow enormously by heating so much so that the whole volume congeals to gel form when kept at suitable temperatures.

The effect of temperature over the sol can be attributed on the property of the colloid particle of giving the adsorbed electrolyte which stabilises the sol in the adsorbed condition. The electrolyte given out by heating renders the sol less stable, more viscous and more conducting. The general belief of colloid chemists (4) has been that a high viscosity of the sol is essentially connected with high hydration of the colloid particle. In this case, the colloid particles seem to loose their adsorptive capacity, thereby, resulting a release of the stabilising ions at a higher temperatures as will be evinced from the electrical conductivity measurements. However, it is not possible to understand how a colloid particle which loses the adsorptive capacity at higher temperatures, is hydrated to a greater extent than a colloid particle which has a high adsorptive power and is less hydrated at a lower temperature. In our opinion the release of adsorbed electrolyte ions decreases the charge of the colloid and thus the structure formation is facilitated which is shown by the increase in the relative viscosity data and remarkable varition of this coefficient with different shearing forces. An increment in the structure of the sol due to this effect may be so high as to congeal it to a gel condition without the addition of any electrolyte.

Thus, the results presented here in this paper as pointed earlier show the fact that the viscosity increases when the temperature is increased and it repeats its value more or less in case of impure sols specially when the measurements are done after warming the sol and then cooling back to the original temperature. In the case of purer samples, however, the viscosity value is not seen to be repeatable by cooling as an increment in the value occures by warming. It appears, therefore, that the viscosity, being a property mostly dependant on the particle size and their structural arrangement is seen to repeat its value when the sol is very impure as

the presence of the peptising ion is in abdunce and thereby it provides very little opportunity for the increment in the viscosity value. As the sols grow pure the colloid particles get the facility of structure formation. The heating of the sol, as has been pointed out earlier makes the colloid particles to lose their adsorptive capacity for ions and the release of electrolyte ions takes place by heating which further makes it unstable and thereby provides more opportunity for the structure formation which may be shown by the increment of the viscosity. The impure samples developing more or less no structure, thus show the repetition in the viscosity value after cooling from a higher temperature to the original one, whilst the pure samples develop the structure by rise of temperature which may not so easily be broken by cooling and hence a permanant increase is seen in the value.

Our results of the measurements of the electrical conductivity of the sols at higher temperature also seem to support the view of the release of the electrolyte impurity by increase in temperature. The conductivity values are not repeatable when the sol is brought back to the original temperature after heating. This can be accounted for the colloid particles may not regain their adsorptive capacity completely because of ageing effect which is enhanced by warming of the sol. Thus the electrical conductivity being mainly dependant over the number of ions and their mobility shows an increment in the value by warming. The view is also supported from the observation in case of purer samples to a more marked degree. In purer samples as the amount of impurity present is considerably low the electrolyte ion contributed from the release from the colloid particles become very significant and hence the effect is seen to be more marked than from the cases of impure samples (Sol AI etc.)

The results here show that the effect is much more pronounced for diluted samples than for the concentrated ones. The adsorbed ions are more easily given out in dilute samples than the concentrated ones as also in dialysis, the presence of excess of water removes the impurities. Dilution as for as the release of the electrolyte is concerned has got the similar influence over the sol as warming.

The view of Kistler (5) about the origin of hydration on the surface of the colloid particle due to the existence of cybotactic complexes in

liquids and the postulation of the cause of the stability of the hydration irrespective of the electric charge over them cannot account for the high viscosity of the sols of iron silicates at higher temperatures as from the above view at higher temperatures the existence of such complexes is less. Further this theory cannot, thus, explain many behaviour of colloids as Kistler himself admits that this cannot be as the main cause of the different observed phenomenon with such colloids.

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ADSORPTION OF BASIC DYES BY COLLOIDAL ROSIN. PART I.

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That certain dyestuffs are adsorbed by materials such as starch kaolin, talc, pumic stone, kiselguhr etc. have been known for a considerable time and the adsorbing properties of these substances have been studied by Suida[1] and Dreaper[2]. Kaolin in particular is one of the best adsorbing agents and its use for the separation of dyestuffs especially when occuring in foodstuffs has been investigated by Chapman and Siedbold[3]. Jamieson and Keyworth[4] and Esters[5] have also studied the adsorption of dyes by kaolin with reference to foodstuffs. As no work has been done on the adsorption of dyes by colloidal rosin, these investigations were undertaken in order to find ultimately some industrial use for the great adsorptive power of rosin for basic dyes which was first observed by the author.

EXPERIMENTAL

2 c. c. of colloidal rosin (7.76 grams of rosin per litre) was taken in each of a number of test tubes and varying amounts of dye solutions and distilled water was added to make the total volume 10 c.c. in each case. The amount of dye solutions added in every case was greater than the amount required for complete coagulation but was less than the amount required for charge reversal. The whole was shaken and was allowed to stand for one hour after which each was filtered through a very small filter paper in order that there might be as little loss of dye from solution as possible due to adsorption by filter paper. The concentration of the dye in the filtrate was determined colorimetrically by comparing them with solutions of known strength. By knowing the amount of dye originally present and determining the equilibrium concentration after adsorption, the actual amount of dye adsorbed by the rosin was calculated.

In order to test if the adsorption of dyes by rosin sols obey the Freundlich's Adsorption Isotherm

$$\frac{x}{m} = a. \, C^{\frac{1}{n}}$$

the values of log C were plotted against log x/m but straight lines were not obtained which proves that the adsorption does not obey the Freundlich's adsorption isotherm. The values of 'x/m' (amount of dye adsorbed expressed in millimoles per gram of rosin) was tabulated against 'C' (concentration of the dye in equilibrium in millimoles per litre) in tables I to VIII and they have been graphically represented in figures I and II.

DISCUSSION

It was observed in most of the cases that when the values of x/m were plotted against 'C', smooth curves showing that there is an increase in adsorption of the dye by rosin with increasing concentration of the dye solution was obtained. But very peculiar curve was obtained for the adsorption of Fuchsine by rosin. In this case the amount of adsorption of the dye by rosin increases with concentration of the dye upto a certain limiting concentration beyond which the adsorption of the dye by rosin decreases. Results of the same type were obtained by Biltz and Steiner[6] for the adsorption of Night Blue and Victoria Blue by cotton, Freundlich[7] for the adsorption of strychnine salts by charcoal or arsenious sulphide and by Dreyer and Sholto[8] for the adsorption of agglutin by bacteria. In all these cases less substance was taken up by the adsorbent from a concentrated solution than from those of medium concentration.

It was observed that basic dyes adsorbed by colloidal rosin could not be washed out easily. This leads to the conclusion that the taking up of basic dyes by colloidal rosin is not guided simply by physical foces of adsorption. Further it has been found that basic dyes are adsorbed more by rosin than acidic dyes. This leads to the conclusion that chemical reaction occurs at the surface of rosin during the taking up of dyestuffs. Moreover the fact that Freundlich's adsorption isotherm is not obeyed for the adsorption of dyestuffs by rosin lends support to this postulate.
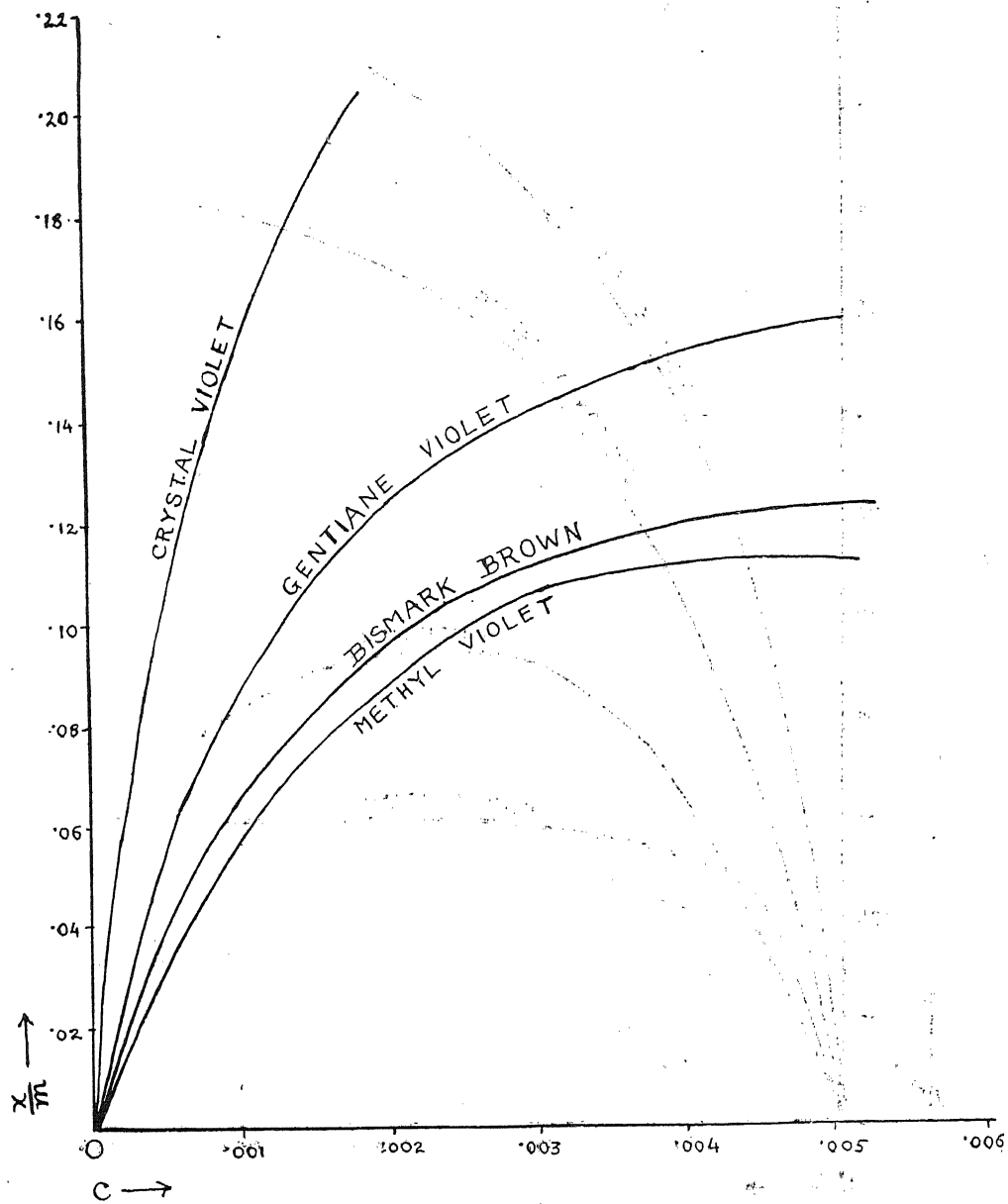
FIG ÷ I
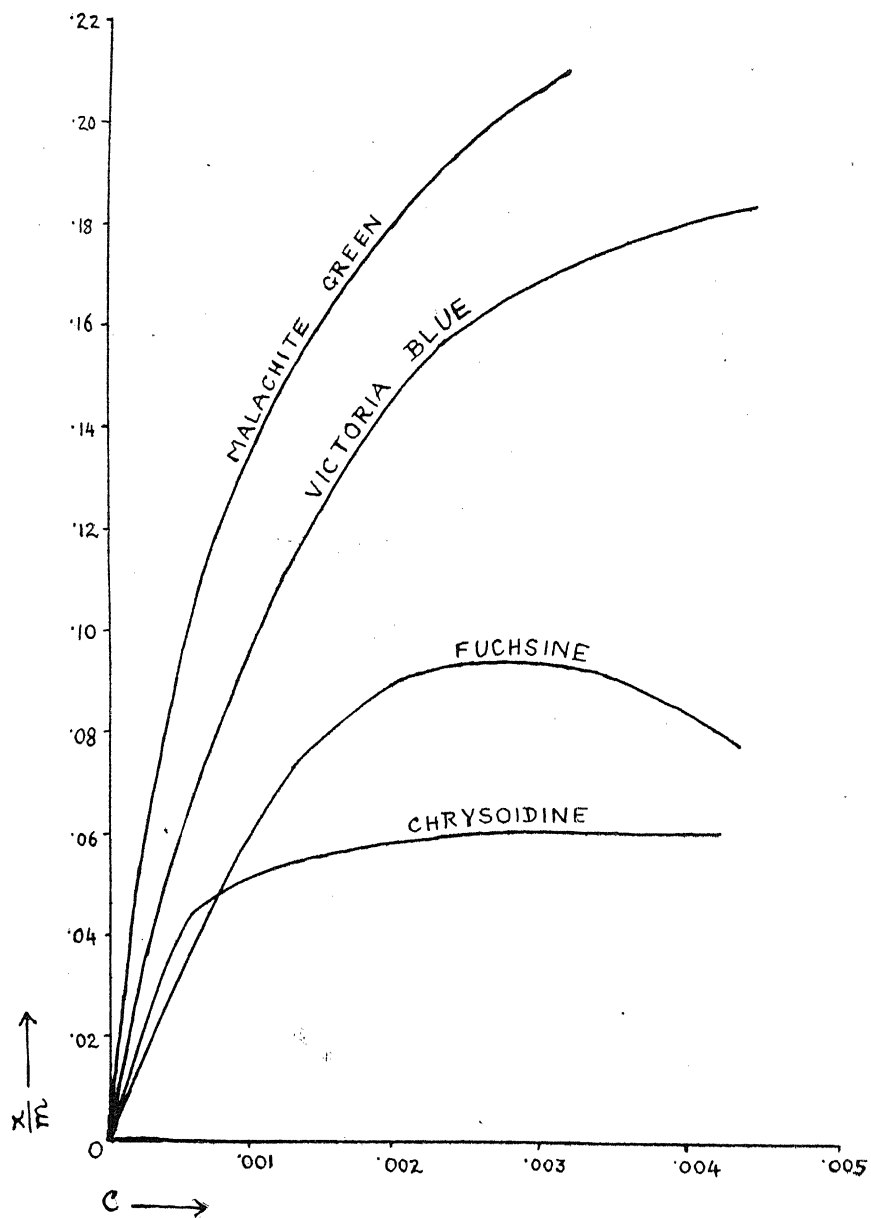
FIG -II

TABLE I
Methyl Violet

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0005021	0.03036
0.0013350	0.07162
0.0018260	0.08516
0.0028220	0.10380
0.0045100	0.11220

TABLE II
Crystal Violet

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0001016	0.03008
0.0002720	0.06024
0.0004810	0.08496
0.0009294	0.15120

TABLE III
Victoria Blue

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0004072	0.04516
0.0006726	0.07536
0.0013040	0.11520
0.0028420	0.16740

TABLE IV
Malachite Green

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0001876	0.04028
0.0004028	0.08035
0.0007296	0.12070
0.0015180	0.16420

TABLE V
Fuchsine

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0005824	0.03514
0.0009978	0.06017
0.0015720	0.07986
0.0035120	0.09602

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TABLE VI

Gentiane Violet

C (Millimoles/litre)	x/m (Millimoles, gram of rosin)
0.0004354	0.05004
0.0011360	0.09500
0.0023310	0.13200
0.0040070	0.15320

TABLE VII

Chrysoïdine

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0004722	0.03506
0.0006828	0.04497
0.0016680	0.05613
0.0031690	0.06211

TABLE VIII

Bismarck Brown

C (Millimoles/litre)	x/m (Millimoles/gram of rosin)
0.0004316	0.03497
0.0009228	0.06319
0.0020420	0.09610
0.0033040	0.11720
0.0046770	0.12090

This fact can be explained by a postulation similar to that of Freundlich and Losev[9] that the base suffers a change, probably into an isomeric modification and becomes insoluble in water. Hantzsch[10] has shown that such transitions also occur when solutions of crystal violet are treated with alkalies.
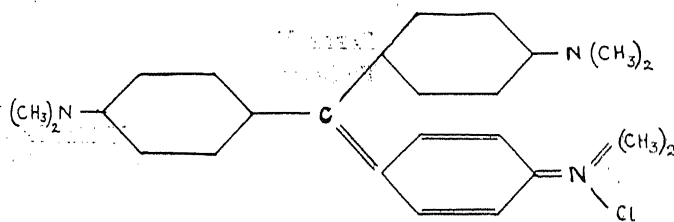
CRYSTAL VIOLET

When equimolecular solutions of crystal violet and potassium hydroxide are mixed, the chlorine ion is replaced by hydroxyl ion and a true soluble base is obtained.
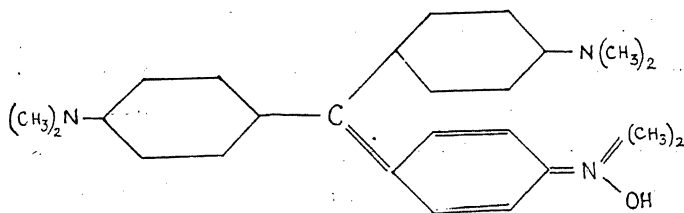
SOLUBLE BASE

This base like the dyestuff is coloured, shows a basic reaction and is therefore dissociated in solution. Gradually the solution becomes colourless, does not react basic and contains the ordinary dyestuff base (Pseudo base) or carbinol.
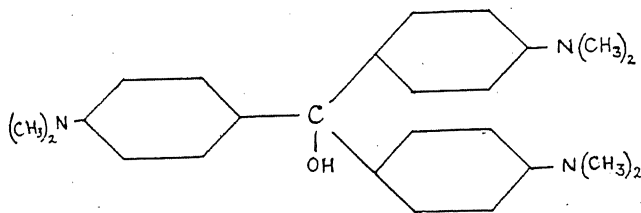
PSEUDO BASE

During adsorption something else also occurs. The adsorbed dyestuff has the same colour as the solution which can be ascribed to a salt formation by the union of dyestuff with rosin. Such a salt formation is not improbable because rosin contains a number of isomeric acids whose general formula is $C_{19}H_{29}COOH$ the carboxyl group of which might unite with the dyestuff base.

Appleyard and Walker[11] have given interesting example of differences in quantitative relations between the adsorption of dyes by fibres on the one hand, a chemical union of the dye with the crystalloid on the other. Freundlich and Losev[12] have studied the adsorption of basic and acidic dyes by charcoal and found that the adsorption of basic dyes-

tuffs differ from that of the acidic ones. In case of basic dyes, chemical action as well as adsorption take place and substances with entirely different properties are formed at the surface of charcoal by chemical reaction.

It is also quite probable that the flocculation of rosin sol acts as a disturbing factor in the adsorption of dyes by rosin. Cameron and Patten[13] finds that the distribution of gentiane violet between soils and water can be represented fairly well by exponential formulas; but that flocculation of the adsorbing medium is apparently a disturbing factor. That flocculation actually takes place had been shown by Patten[14] in a special set of experiments on quartz flour and dyes.

It was also observed that very finely powdered rosin was capable of adsorbing the basic dyes. But on comparing the adsorption obtained with the sol and with powdered rosin, it was found that in general the adsorption of dyes are greater with the sol than with the powder. This is, as is expected and the difference is mainly due to the ion necessary to neutralize the charge on the sol. Further it has already been shown by the author[15] that greater the coagulating power of the basic dyes for the rosin sol, the less is the actual amount of adsorption by the rosin.

The chemistry of adsorption is not simple for the chemical surface of the colloids is not exactly known. Since, for example, according to Freundlich, the surfaces of the particles in a sulphur sol prepared by the method of Oden consist of a polythionic acid, so may we also expect that other simple or even elementary colloids should exhibit a complex condition at their surface.

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RADIAL PULSATIONS OF THE TWO STELLAR MODELS

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SUMMARY

[Radial oscillations of the two stellar models in which the density is proportional to (1) $1-r/R$ and (2) $1-r^2/R^2$, respectively, have been considered. A method as developed by Ledoux and Pekeris using Rayleigh's principle has been applied to find the periods of the fundamental mode of oscillation for both the models. It is found that the method gives in the first case a lower value for the fundamental period, while in the second case better result for the fundamental period is obtained. The period and amplitude of oscillation for the first model is also found out.]

The investigation of various stellar models with different density distribution were studied by Eddington[2], Sterne[5], and others. As it is of interest to consider the law of density in such a way that it vanishes at the surface of the star and with no central singularity, the following laws of density have been considered for the two stellar models :

$$(1) \quad \rho = \rho_c \left(1 - r/R\right).$$

$$(2) \quad \rho = \rho_c \left(1 - r^2/R^2\right).$$

where ρ is the density at any point r, ρ_c is the central density, and R is the radius of the star.

In order to find the period and amplitude of oscillation for these two models we have followed the general method given by Ledoux[3] and Pekeris who applied Rayleigh's principle to derive approximate values ·for the fundamental period of radial oscillation of a non-rotating star, as their results show that quite good approximations to the period could be obtained by assuming simple formulae for the displacement during the oscillation.

The differential equation for small radial oscillation as given by Eddington[1], is

$$\frac{d^2\xi}{dr^2} + \frac{4-\mu}{r}\frac{d\xi}{dr} + \left(\frac{\sigma^2\rho}{\gamma P} - \frac{\alpha\mu}{r^2}\right)\xi = 0 \qquad (1)$$

where ξ is the amplitude of displacement $\frac{\delta r}{r}$, g, ρ, P being respectively the undisturbed values of gravity, density, and pressure at a distance r from the centre, $\mu = \frac{g\,\rho\,r}{P}$ and $\alpha = 3 - 4/\gamma$, γ being the ratio of specific heats, $\sigma = \frac{2\pi}{\tau}$ where τ is the period of pulsation. We shall change the equation (1) to a convenient form by multiplying with γ Pr, and we get,

$$\chi r \frac{d^2\xi}{dr^2} + \left(4\chi + r\frac{d\chi}{dr}\right)\frac{d\xi}{dr} + \left[\left(\sigma^2 + \frac{4Gm(r)}{r^3}\right)\rho r + \frac{3d\chi}{dr}\right]\xi = 0 \qquad (2)$$

where $\chi = \gamma$ P, m (r) is the mass interior to r, and $\frac{dP}{dr} = -\frac{Gm(r)}{r^2}\rho$. Again multiplying equation (2) by r^3, it can be put in the self-adjoint form

$$\frac{d}{dr}\left(\chi r^4\frac{d\xi}{dr}\right) + \left[\sigma^2 r^4\rho + 4Gm(r)r\rho + 3r^3\frac{d\chi}{dr}\right]\xi = 0 \qquad (3)$$

The boundary conditions

$$\delta r = 0 \text{ at } r = 0.$$

$$\delta P = -\gamma P\left(3\xi + \frac{rd\xi}{dr}\right) = 0 \text{ at } r = R, \qquad (4)$$

are met if ξ is regular in the range of integration.

Equation (3) is the Eulerian equation of the variational problem of minimizing the integral

$$J = \int_0^R \left[\chi r^4\,\xi'^2 - \left\{4Gm(r)\rho r + 3r^3\frac{d\chi}{dr}\right\}\xi^2 - \sigma^2\xi^2\rho r^4\right]dr. \qquad (5)$$

The conditions of this free variational problem are

$2\chi r^4\xi' = 0$ at $r = 0$ and at $r = R$, both of which are satisfied by equations (4). The minimum value of this integral is σ_0^2, where

$$\sigma_0^2 = \min \frac{\int_0^R \gamma P r^4\xi'^2\,dr + \int_0^R (3\gamma - 4)\xi^2 Gm(r)r\rho\,dr}{\int_0^R \xi^2\rho r^4\,dr} \qquad (6)$$

These are the same equations as have been obtained by Ledoux[3] and Pekeris.

Now we consider the two cases.

Case I.

$$\rho = \rho_c \, (1 - r/R). \qquad \qquad \qquad \qquad (7)$$

Changing to independent variable

$$x = r/R,,$$

and with the law of density given by (7) we have

$$m \, (r) = \frac{\pi \rho_c}{3} \, (4\text{-}3x) \, R^3 \, x^3,$$

$$g \;\; = \frac{\pi G \rho_{c_1}}{3} \, (4\text{-}3x) \, Rx,$$

$$P \; = \frac{\pi G \rho_c^2 \, R^2}{36} \, \{5\text{-}24x^2 + 28x^3\text{-}9x^4\},$$

$$\mu \; = \frac{12x^2 \, (4 - 3x)}{(1 - x) \, (5 + 10x - 9x^2)}.$$

$$\text{and} \; \frac{R^2 \rho}{P} = \frac{36}{\pi G \rho_c (1 - x) \, (5 + 10x - 9x^2)}. \qquad \qquad (8)$$

Substituting these values in equation (1) we get the differential equation

$$x(1-x) \, (5 + 10x - 9x^2) \frac{d^2\xi}{dx^2} + (20 + 20x - 124x^2 + 72x^3) \frac{d\xi}{dx} + \{F - 12\alpha(4 - 3x)\}x\xi = 0, \; (9)$$

$$\text{where } F = \frac{36\sigma^2}{\pi G \rho_c \gamma} \qquad \qquad \qquad (10)$$

Equation (9) has regular singularities at the origin, and at $x = 1$. The roots of the indicial equation are 0 and -3, we retain only the former value to avoid singularity at the centre. Assuming a solution in series

$$\xi = \sum_{k=0}^{\infty} b_k x^k,$$

we find the various coefficients as follows :

$$b_1 = 0,$$

$$50 \, b_2 + (F - 48\alpha) \, b_0 = 0 \, ;$$

$$90 \, b_3 + 50 \, b_2 + 36\alpha \, b_9 = 0,$$

$$140 \, b_4 + 90 \, b_3 - \{286 - (F - 48\alpha)\} \, b_2 = 0,$$

$$200 \, b_5 + 140 \, b_4 - \{486 - (F - 48\alpha)\} \, b_3 + (162 + 36\alpha) \, b_2 = 0, \qquad , \qquad , \qquad . \quad (11)$$

$$5 \, (n^2 + 5n + 4) \, b_{n+1} + (5n^2 + 15n) \, b_n - \{19n^2 + 67n - 86 - (F - 48\alpha)\} b_{n-1}$$
$$+ \, (9n^2 + 27n - 90 + 36\alpha)\} \, b_{n-2} = 0 \qquad . \qquad , \qquad , \qquad . \quad (12)$$

where n is a positive integer.

We shall find the period for the fundamental mode by minimizing the integral given by equation (5) and applying Ritz method to obtain higher approximations for the fundamental period. Assume

$$\xi = a_0 + a_1 \, x + a_2 \, x^2 \dots \qquad \qquad (13)$$

where $\qquad \qquad x = r/\text{R}$

substituting equations (7), (8), and (13) in equation (5), we get

$$J = \frac{\pi G \rho_c^2 \gamma \text{R}^5}{36} \int_0^1 \; [\; x^4 \, (5 - 24x^2 + 28x^3 - 9x^4) \, (a_1 + 2a_2 \, x)^2$$

$$+ \; \{12\alpha \, x^4 \, (4 - 7x + 3x^2) \, - \, \beta \, (1 - x) \, x^4\} \, (a_0 + a_1 x + a_2 x^2)^2]dx \qquad . \qquad (14)$$

where $\quad a = 3 - 4/\gamma,$

$$\text{and } \beta = \frac{36\sigma^2}{\pi G \rho_c \gamma} = \text{F}$$

the coefficients a_0, a_1, a_2, are determined by the three equations of the form

$$\frac{\partial J}{\partial a_j} \; 0, j = 0, 1, 2.$$

and so we have

$$\left(\frac{26\alpha}{35} - \frac{\beta}{30} \right) a_0 + \left(\tfrac{1}{2}\alpha - \frac{\beta}{42} \right) a_1 + \left(\frac{5\alpha}{14} - \frac{\beta}{56} \right) a_2 = 0,$$

$$\left(\tfrac{1}{2}\alpha - \frac{\beta}{42} \right) a_0 + \left(\frac{1+5\alpha}{14} - \frac{\beta}{56} \right) a_1 + \left(\frac{4+12\alpha}{45} - \frac{\beta}{2} \right) a_2 = 0,$$

$$\left(\frac{5\alpha}{14} - \frac{\beta}{56} \right) a_0 + \left(\frac{4+12\alpha}{45} - \frac{\beta}{72} \right) a_1 + \left(\frac{136+238\alpha}{1155} - \frac{\beta}{90} \right) a_2 = 0. \quad \dots \quad (15)$$

The first approximation for the fundamental mode of vibration corresponds to $\xi = $ constant, and we get $\beta = 13.37$, for $\gamma = \tfrac{5}{3}$

The second approximation will consist in taking $\xi = a_0 + a_1 \, x$, a quadratic equation of the second-degree is obtained in β, the smaller root gives the second approximation. The third approximation corresponds to $\xi = a_0 + a_1 x + a_2 x^2$, a cubic equation in β is obtained, and this cubic equation has been solved approximately by Horner's method.

The value of F is given in the tabular form for $\gamma = 5/3$.

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TABLE I.

α	Fundamental Mode of Vibration		
	First App.	Second App.	Third App.
0.6	13.37	13.23	13.21

If we substitute this value of F in equations (11) we find that the values of all the coefficients go on increasing without limit, so the series obtained for these values of the coefficients will be a divergent one. Thus recourse had to be taken to other method of finding the value of F such that we may get a convergent series. Though no method has yet come out to solve a difference equation with four coefficients as equation (12), so we tried by successive trials to find out F such that the coefficients in equation (11) may go on decreasing. Curiously enough it was not much difficult to find such a vlaue of F for equation (12). We have found that for $F = 35.57617$, the coefficients in equation (11) go on decreasing after some fixed term. The series obtained with these values of coefficients in terms of b_0 is as follow :

$$\xi = b_0 \{1 - .135523x^2 - .164709x^3 - .164410x^4 - .155165x^5 - .143913x^6$$
$$- .133141x^7 - .123606x^8 - .115535x^9 - .108617x^{10} \ldots \ldots\} \qquad . \qquad . \quad (16)$$

The value of F obtained by applying Rayleigh's principle for this model is appreciably low. It is obtained due to the sensitivity of the method to slight numerical errors. We come to the same conclusion for this model, as have been drawn by Cowling and Newing that ' an over-elaborate use of Rayleigh's principle was prone to give misleading results'.

But quite contrary to this has been obtained for the second model, where applying Rayleigh's principle, the value of F gives quite good approximations as will be seen later. The value of F for the first model $\rho = \rho_c (1 - r/R)$, which is 35.57617 gives a convergent series (equation 16) with all the terms negative except the first. So it is difficult to say anything precisely at this stage about the stability of this particular model. We need further investigation before giving any verdict about the stability of this particular model.

Case II.

$$\rho = \rho_c \, (1 - r^2/R^2). \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (17)$$

Radial oscillations of this model has already been considered by Chandrika Prasad[4], who has found out the solutions for the periods and amplitudes of the fundamental and higher modes by a method used by Kelvin and Darwin for tides on a rotating globe. Our results obtained for the period and amplitude of the fundamental mode by Rayleigh's principle are practically the same.

With the law of density as given by the equation (17) we have

$$m\,(r) = \frac{4}{15}\, \pi\rho_c\, (5 - 3x^2)R^3x^3,$$

$$g = \frac{4}{15}\, \pi G\rho_c\, (5 - 3x^2)\, Rx,$$

$$P = \frac{4}{15}\, \pi G\rho_c{}^2 \left(1 - \frac{5}{2}\, x^2 + 2x^4 - \tfrac{1}{2}\, x^6\right) R^2,$$

$$\mu = \frac{2x^2\,(5 - 3x^2)}{(1 - x^2)(2 - x^2)},$$

$$\text{and} \quad \frac{R^2\rho}{P} = \frac{15}{2\pi\rho_c G\,(1 - x^2)\,(2 - x^2)} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (17a)$$

where $x = \dfrac{r}{R}$.

With these substitutions the equation (1) becomes

$$x(1 - x^2)(2 - x^2)\,\frac{d^2\xi}{dx^2} + (8 - 22x^2 + 10x^4)\frac{d\xi}{dx} + \{F - 2\alpha\,(5 - 3x^2)\}x\xi = 0. \qquad . \quad (18)$$

$$\text{where } F = \frac{15\sigma^2}{2\pi\rho_c\gamma G} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \quad (19)$$

The equation (18) has regular singularities at the origin, and at $x = 1$. We do not consider $x = \sqrt{2}$ as it lies outside the star.

The roots of the indicial equation are o and -3. To avoid singularity at the origin we must choose the former. Assuming a solution in series.

$$\xi = \sum_{k=0}^{\infty} b_k x^k$$

we find that the odd coefficients vanish and the even coefficients are given by

$$20b_2 + (F - 10\alpha)\, b_0 = 0,$$
$$56b_4 - \{50 - (F - 10\alpha)\}\, b_2 + 6\alpha\, b_0 = 0 \qquad . \qquad . \qquad . \qquad . \qquad . \quad (20)$$

$$2 \, (2n+2) \, (2n+5) \, b_{2n+2} - \{ 2n \, (6n+19) - (F - 10\alpha) \} \, b_{2n}$$
$$+ \{ 2 \, (2n+7) \, (n-1) + 6\alpha \} b_{2n-2} = 0 \; . \qquad . \quad (21)$$

-where n is a positive integer.

Now, we shall find the period the fundamental mode by minimizing the integral given by the equation (5), applying Ritz method for higher approximations. Assuming

$$\xi = a_0 + a_1 x^2 + a_2 x^4 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (22)$$

where x=r/R, and substituting (17), (17a), and (22) in equation (5) we get

$$J = \frac{2}{15} \pi \gamma G \rho_c{}^2 \, R^5 \int_0^1 [x^4 \, (2 - 5x^2 + 4x^4 - x^6) \, (2a_1 x + 4a_2 x^3)^2$$

$$+ \{ 2\alpha x^4 \, (5 - 3x^2) \, (1 - x^2) - \beta x^4 \, (1 - x^2) \} \, (a_0 + a_1 x^2 + a_2 x^4)^2] dx \; . \qquad . \quad (23)$$

where $\quad \alpha = 3 - 4/\gamma$, and $\beta = \dfrac{15\sigma^2}{2\pi G \rho_c \gamma} = F \qquad . \qquad . \qquad . \qquad . \qquad . \quad (24)$

the three coefficients are determined by the three equations of the form

$$\frac{\partial J}{\partial a_j} = 0, \, j = 0, \, 1, \, 2.$$

the three equations are found to be

$$\left(\frac{8\alpha}{21} - \frac{2}{35} \, \beta \right) a_0 + \left(\frac{136\alpha}{693} - \frac{2}{63} \, \beta \right) a_1 + \left(\frac{152\alpha}{1287} - \frac{2}{99} \, \beta \right) a_2 = 0$$

$$\left(\frac{136\alpha}{693} - \frac{2}{63} \, \beta \right) a_0 + \left(\frac{608 + 1064\alpha}{9009} - \frac{2}{99} \, \beta \right) a_1 + \left(\frac{1344 + 1512\alpha}{19305} - \frac{2}{143} \, \beta \right) a_2 = 0,$$

$$\left(\frac{152\alpha}{1287} - \frac{2}{99} \, \beta \right) a_0 + \left(\frac{1344 + 1512\alpha}{19305} - \frac{2}{143} \, \beta \right) a_1 + \left(\frac{2944 + 2024\alpha}{36465} - \frac{2}{195} \, \beta \right) a_2 = 0$$

$$. \qquad . \qquad . \quad (25)$$

As before, the first, second and third approximations are found out and they are given in the tabular form in Table II

TABLE II.

α	Fundamental Mode of Vibration		
	First App.	Second App.	Third App.
0.6	4.00000	3.97803	3.97547

Putting this value of F in equation (20) we get the values of all the coefficients, and the series is found to be

$$\xi = b_0 \{1 + \cdot10123x^2 + \cdot09405x^4 + \cdot08569x^6 + \cdot07978x^8 + \cdot07524x^{10} + \ldots\} \quad . \quad . \quad (26)$$

Table III gives a comparison of the periods of this second model obtained by the application of Rayleigh's principle, with that found by Chandrika Prasad using some other method, for $\gamma = 5/3$.

TABLE III

Values of F for the model $\rho - \rho_c\left(1 - \dfrac{r^2}{R^2}\right)$

α	As found out by our method from third approx.	As found out by Chandrika Prasad.
0·6	3.97547	3.97756

Thus in the second case we see that Rayleigh's principle gives quite good approximations to the period of the fundamental mode.

I wish to express my grateful thanks to Prof. A.C. Banerji for his keen interest in this paper. I am also indebted to Dr. P. L. Bhatnagar for his help and suggestions for improvement.

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THE RELATIVE INFLUENCE OF SURFACE AND BACTERIAL OXIDATIONS IN THE FIXATION OF NITROGEN

By N. R. Dhar, B. G. Chatterji, N. N. Pant & B. B. L. Saxena

From a careful consideration of the experimental results obtained by different workers in this Laboratory it appears that the transformations of organic substances, when mixed with .soil, are primarily surface and catalytic reactions accelerated by light absorption. The part played by micro-organisms is of a secondary nature. The following observations have been made by B. G. Chatterji :—

250 gms. of soil+40 gms. of cowdung. (Unsterile)   *LIGHT.*

Date	Total carbon in 100 gms. of soil in gm.	Total nitrogen in 100 gms. of soil in gm.	Azotobacter count in million per gm. of dry soil	Efficiency i.e., amount of nitrogen fixed in mgms. per gm. of carbon oxidized
3–1–47.	1.476	0.0931	2.5	..
5–3–47.	1.212	0.0986	18.0	21.0
3–5–47.	1.001	0.1029	39.0	20.0
Do.	..	Do.	Do.	*DARK*
5–1–47.	1.460	0.0924	2.5	..
0–3–47.	1.310	0.0942	72	11.8
5–5.47.	1.181	0.0955	135	10.0
Do.	..	Do.	Do. (Sterile)	*LIGHT*
8–1–47.	1.442	0.0916	..	..
10–3–47.	1.277	0.0941	..	15.4
9–5–47.	1.139	0.0962	..	15.0
Do.	..	Do.	Do.	*DARK*
10–1–47.	1.460	0.0924	..	..
12–3–47.	1.370	0.0932	..	8.8
11–5–47.	1.285	0.0939	..	8.2

From the above observations it is evident that under unsterile conditions, the carbon of cowdung decreases from 1.46 to 1.18% in four months, i. e., a fall of 0.28% in dark whilst in light, the fall is from 1.476 to 1.001%, i. e., 0.475%. Under sterile conditions, in the dark, the fall is, in the same period, from 1.460 to 1.285%, i. e., 0.175% and in light it is from 1.442 to 1.139%, i. e., 0.303%. It is clear, therefore, that the oxidation of 0.175% carbon of cowdung under sterile conditions in the dark is certainly a surface and catalytic oxidation, whilst in presence of all kinds of micro-organisms the total oxidation in the dark is 0.28%. If we subtract the first (0.175%) from the second (0.28%) we can obtain the effect of micro-organisms alone, i.e., 0.105%. In other words, even in cowdung which is rich in micro-organisms the surface action is much greater than the micro-organic oxidation. To rule out the intricacies involved in the sets exposed to sunlight, we have here considered the sets of experiments performed in the dark only where surface, catalytic and micro-organic oxidation may be the only factors contributing towards total oxidation under unsterile conditions, while surface and catalytic oxidation shall contribute towards total oxidation under sterile conditions.

Summarising the experimental results obtained with other energy materials, the following values regarding the relative influence of surface and microbial oxidations are obtained :—

Cowdung		Neem Leaf		Wheat Straw		SANAI (sun hemp.)	
Surface oxdtn.	Microbl. oxdtn.	Surface oxdtn.	Microbl. oxdtn.	Surface oxdtn.	Mircobl. oxdtn.	Surface oxdtn.	Microbl. oxdtn.
175	105	287	55	166	151	142	78
(a) 165	99	521	100				
135	79	271	44	148	138	134	54
(b) 170	100	615	100				
105	63	221	27				
(c) 166	100	819	100				

All these results show that the surface oxidation is more active than the microbiological action. The case of Neem (Melia Azadiractta Lina)

Leaf is quite interesting in that the microbiological action is exceedingly small in comparison with the surface oxidation. This is perhaps due to the bactericidal property of the Neem Leaf.

N. N. Pant has recorded some interesting results on the oxidation of Inulin, Leaves, Cowdung, Molasses etc. in sterile and unsterile conditions. His results, when summarised in identical manner, are as follows :—

IN DARK

Inulin		Leaves		Cowdung		Molasses	
Surface oxdtn.	Microbl oxdtn.	Surface oxdtn.	Microbl oxdtn.	Surface oxdtn.	Microbl oxdtn.	Surface oxdtn.	Microbl oxdtn.
357	52	187	34	206	45	322	86
329	54	171	14	193	44	305	87
373	57	209	38	217	56	338	93
288	40	122	11	161	35	287	76

The foregoing results obtained by Pant show clearly that the surface oxidation is much greater than the microbiological oxidation not only with soils but with other surfaces as well.

B. B. L. Saxena has studied the oxidation of different energy materials like starch, Ghee (melted butter) and other substances using chemically pure substances like aluminium phosphate, chromium phosphate, calcium phosphate, aluminium oxide, ferric oxide, nickel oxide etc. as surfaces in place of soil. His observations are as follows :—

Experiments with Calcium Phosphate+Starch

Started on 24-7-47   *I Analysed on* 24-9-47 *Period of Exposure* 2 months

Conditions.	Total C. in gm. (Initial) %	Total N. in mgm. (Initial) %	Total C. in gm. (Unoxdsd.) %	Total C. in gm. (Oxdsd.) %	Gain Total Nitrogen in mgm. %	Efficiency
			STERILE			
Exposed.	1.0000	Nil.	0.7707	0.2293	5.8_7	25.6
Covered.	1.0000	,,	0.8900	0.1100	1.3_2	11.98
Exposed.	0.5000	,,	0.3505	0.1495	4.3_2	28.8
Covered.	0.5000	,,	0.4301	0.0699	0.9_8	14.08

Experiments with Calcium Phosphate+Starch

Started on 24-7-47 I *Analysed on* 24-9-47 *Period of Exposure* 2 months.

UNSTERILE

Exposed.	1.0000	Nil.	0.4972	0.5028	24.1$_1$	47.9
Covered.	1.0000	,,	0.7624	0.2376	5.5$_8$	23.48
Exposed.	0.5000	,,	0.1971	0.3029	16.4	54.1
Covered.	0.5000	,,	0.3778	0.1222	3.0$_2$	24.7

Experiments with Calcium Phosphate+Starch

Started on 24-7-47 II *Analysed on* 21-12-47 *Period of Exposure* (5 months)

STERILE

Conditions	Total C. in gm. (Initial) %	Total N. in mgm. (Initial) %	Total C. in gm. (Unoxdsd.) %	Total C. in gm. (Oxdsd.) %	Gain Total Nitrogen in mgm. %	Efficiency
Exposed.	1.0000	Nil.	0.5218	0.4782	13.0	27.1
Covered.	1.0000	,,	0.7500	0.2500	3.3	13.2
Exposed.	0.5000	,,	0.2312	0.2688	9.0	33.4
Covered.	0.5000	,,	0.3578	0.1422	2.5	17.5

Experiments with Calcium Phosphate+Starch

Started on 24-7-47 II *Analysed on* 21-12-47 *Period of Exposure* (5 months)

UNSTERILE

Exposed.	1.0000	,,	0.4000	0.6000	25.0	41.6
Covered.	1.0000	,,	0.6625	0.3375	6.8$_8$	20.4
Exposed.	0.5000	,,	0.1500	0.3500	16.8	48.0
Covered.	0.5000	,,	0.3046	0.1954	4.0	20.4

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From the foregoing results it is evident that the bacterial oxidation is much less than the surface oxidation. Besides these experiments, a large number of experiments have been performed with different energy materials using other chemically pure substances as surface which strongly support the view that surface plays a much more important role than the micro-organisms in the process of oxidation of energy materials, even in the dark.

Summarising the results of this type of experiments, the following relative values have been obtained :—

IN DARK

Surface oxidation	Microbial oxidation	GHEE.
168.4	116	
124	54	
200	55	
118	25	
210	143	
151	71	
250	66.6	
147	30.6	

Starch. (Aluminium Phosphate as Surface)

108	68
162	78
144	76
213	105

Starch. (Chromium Phosphate as Surface)

79.5	41.5
141	63
110	56
200	73

Starch. (Calcium Phosphate as Surface) *In DARK.*

Surface oxidation.	Microbial oxidation
70	52
250	87
142	52

Starch. (Nickel oxide as Surface)

140	14
88.5	17.5

Starch. (Iron oxide as Surface)

138	52
93.2	48

Starch. (Zinc oxide as Surface)

135	60
81	44

Starch. (Aluminium oxide as Surface)

95.5	49
150	53

Glucose. (Soil as Surface)

Amount of Surface

5 gms.	128	37
1 ,,	111	52

Glucose. (Zinc oxide as Surface)

50 ,,	160	30
5 ,,	101	28
1 ,,	88	28

Glucose. (Aluminium oxide as Surface)

50 ,,	132	26
5 ,,	90	24
1 ,,	86	20

Glucose. (Iron oxide as Surface)

50 ,,	143	23
5 ,,	93	26
1 ,,	86	22

Glucose. (Nickel oxide as Surface)

50 ,,	144	29
5 ,,	97	22
1 ,,	82	30

Glucose. (Calcium Sulphate as Surface)

50 ,,	116	50
5 ,,	84	38
1 ,,	76	39

Glucose. (Barium Sulphate as Surface)

50 ,,	114	50
5 ,,	79	42
1 ,,	78	44

Glycerol. (Chromium Phosphate as Surface)

Amount of Surface	Surface oxidation	Microbial oxidation
50 gms.	143	40
5 "	113	23
1 "	103	22

Glycerol. (Iron Phosphate as Surface)

50 "	158	45
5 "	126	33
1 "	117	31

Glycerol. (Aluminium Phosphate as Surface)

50 "	159	44
5 "	129	27
1 "	117	23

Glycerol. (Calcium Phosphate as Surface)

50 "	164	46
5 "	125	41
1 "	111	36

Glycerol. (Titania as Surface)

50 "	178	33
5 "	107	40
1 "	94	41

A careful study of the foregoing results brings out the marked significance of surface in oxidation reactions. In almost all these results the surface oxidation is much greater than the microbial oxidation. Another interesting point of considerable importance is brought out by these experiments that as the amount of surface is increased, the values for surface oxidation are markedly increased, keeping the microbial oxidation values more or less the same. For instance, when zinc oxide is used as a surface and glucose as energy material, the ratio of surface oxidation : microbial oxidation is 160 : 30 when 50 gms. of the surface have been introduced, whilst the same ratio goes down to 88 : 28 when only 1 gm. of the surface is used. Thus, the surface oxidation shoots up from 88 to 160 as the amount of surface is increased from 1 gm. to 50 gms., but there is no such effect on the microbial oxidation in which

case the values keep more or less constant, being 28 with 1 gm. of surface and only 30 even when the amount of surface is increased to 50 gms. Similar results have been obtained when with iron oxide as surface and the same energy material the ratios are 143 : 23 and 86 : 22 with 50 gms. and 1 gm. as surface respectively. Or, in the case of nickel oxide the ratios are 144 : 29 and 82 : 30 when the amount of surface has been raised from 1 gm. to 50 gms.

In recent years Dr. Jensen, Dr. Stöckli and others have expressed the opinion that Azotobacter does not play a big role in increasing the nitrogen status of soils in cold countries. Professor Lemoigne of Paris is of the opinion that Azotobacter is of no help in improving the soil nitrogen in France. These views are in direct support of the conclusion drawn above in connection with experiments carried out by us. If bacterial action is not as prominent as surface reaction, then their existence or non-existence should not materially affect the nitrogen status of the soil and the oxidisability of the organic compound added to the soil. It appears that the microbiological action is vigorous either in culture media containing easily decomposable energy materials or in sewage or in fermentation reactions. On the other hand, if the energy materials to be utilized by the bacteria and the bacterial population are diluted or mixed up with large quantities of inert and difficultly soluble materials like sand, soil, iron oxide, zinc oxide, nickel oxide, calcium sulphate, barium sulphate etc. the intensity of the bacterial action decreases. In most experiments for the isolation or detection of bacteria the conditions are rendered suitable for their rapid multiplication by supplying energy materials for their growth and activity and mineral food requirements. This is why Azotobacter or *Clostridia* have been found to multiply and fix nitrogen in tubes or flasks. But under natural conditions, in soil or sand, the amount of nitrogen fixed by additions of energy materials has not been determined in cold countries.

Sir John Russell and Profesor Waksman are of the opinion that the non-symbiotic bacteria are of small use in increasing the nitrogen status when energy materials are added to the soil in cold countries. On the other hand, the fixation of nitrogen by symbiosis of plants like lucerne, clover, sunhemp, peas etc. and rhizobium takes place in a compact condi-

tion in the root nodules of the plants. The bacterial food is produced by the plants chiefly as carbohydrates which pass through the stem into the nodules where they come in contact with the bacteria and fix atmospheric nitrogen. In culture experiments in flasks containing energy materials like glucose, mannitol etc. and minerals like lime, potash, iron and phosphate etc. the system is very compact and the energy materials are readily available to the bacteria in a state of solution. On the other hand, even if 10 tons of molasses are added per acre of land, it is diluted with 99% of its weight of the inert silicates, iron oxide, moisture etc. present in the soil, and hence the chance of bacteria and the food material to come in contact with each other appears to be much less than in the culture media in flasks where, due to the movement of the dissolved material, there are frequent collisions between the bacteria and their food materials, and hence the possibility of the growth and activity of bacteria is greater in culture media than in natural conditions in the soil. It is clear, therefore, that the chemical changes involved in bacterial reactions with energy materials are bound to be slower in soil than in culture media. Thus the chemical changes in soil, under ordinary conditions, are much slower, and that is why on adding organic matter to the soil a definite time interval is necessary before the oxidation and nitrogen fixation are observed. In cold countries this process is slower than in warm countries. Moreover, in cold countries, the nitrogen status of soils is higher than in warm countries and the apparent nitrogen fixation on adding energy materials will be less prominent than in hot countries. It appears that the nitrogen status of soils of all countries not under legumes appears to be chiefly due to the surface and photo oxidation of all kinds of energy materials and consequent nitrogen fixation.

It is well known that sugars, alcohols, sodium or potassium salts of organic acids have been used as energy materials in the fixation of atmospheric nitrogen by Azotobacter and *Clostridia* in culture systems. But these bacteria are not capable of fixing the nitrogen by addition of cellulosic or lignin materials. The generally accepted view is that the cellulose decomposing organisms first break up cellulose into soluble carbohydrates which are utilisable by the nitrogen fixers. It seems that

the activity of the cellulose decomposing bacteria will be decreased by the addition of sand or soil.

Schloesing and Muntz have shown that the nitrification of sewage is practically stopped by adding chloroform. This is because under ordinary conditions, the nitrification of the nitrogenous matter present in sewage is a biological process and not a surface action. On the other hand, if a large quantity of sand or soil is added to the sewage, the oxidation becomes a surface reaction and chloroform cannot stop the nitrification. The beneficial effect on the nitrification caused by partial sterilization of the soil appears clear from the surface oxidation point of view, because, on partial sterilization, the aeration and surface reaction increase. Moreover, our experiments on nitrogen fixation, observed with all types of energy materials including coal, are more readily explicable from the surface oxidation viewpoint rather than from the microbial viewpoint. The observations of Broadbent, showing that the addition of Sudan grass helps in the oxidation of the soil humus, can also be explained from the increase in the surface of the system. Similarly, our results, showing greater oxidation of sugar or straw when mixed with coal, are also clear from the same viewpoint.

Phenols are known to undergo oxidation in Rothamsted soils. Similarly, antiseptics like sodium benzoate, sodium salicylate etc., have been oxidised in our soils. These can be explained easily from the surface oxidation viewpoint rather than from the bacterial one.

Dr. H. L. Jensen (Proc. Linn. Soc. New South Wales **65**, 1 (1940) thought that a time interval of only 30 days will be quite adequate in his experiments of nitrogen fixation with Australian soils using glucose as an energy material. He must have been under the impression that the whole process is entirely bacterial and would be quick. He expected that the bacteria (Azotobacter) would be multiplied very rapidly and eat up the glucose and in this process nitrogen fixation will be observed. But he did not obtain any nitrogen fixation in most of his experiments and concluded that Australian soils cannot fix nitrogen even in the presence of Azotobacter. It appears that 30 days' incubation at 30° is too short a time, and if he had given a time interval of 2 or more months, he would have obtained some nitrogen fixation as we have done.

SUMMARY

Experimental results show that marked nitrogen fixation takes place when soil or insoluble substances like ferric oxide, zinc oxide, aluminium oxide, titania, nickel oxide, calcium sulphate, calcium phosphate etc. are mixed with energy materials like cowdung, leaves, starch, glucose, glycerol, ghee (melted butter) and inulin and allowed to undergo slow oxidation in air both in the sterile and unsterile conditions. The nitrogen fixation in sunlight is much greater than in the dark.

The surface oxidation of these energy materials is more pronounced than the microbial oxidation.

EFFICIENCY OF DIFFERENT METHODS OF NITROGEN FIXATION

By N. R. Dhar, S. M. Bose, S. B. Sinha and S. K. Ghosh

Industrial Processes of Nitrogen Fixation.—It is well known that H. Cavendish was the first to fix atmospheric nitrogen in the laboratory by passing electric spark through air in 1783. In 1893 Lord Rayleigh isolated argon from air by confining a mixture of nine volumes of air and eleven volumes of oxygen in a glass globe in which an electric flame was produced. Lord Rayleigh obtained 49 grams of nitric acid per kilo watt hour. The yield of nitric acid can be increased to 88 grams by modifying the nature of the arc discharge. In 1903 K. Birkeland and S. Eyde established a factory at Notoddem, Norway, for the fixation of atmospheric nitrogen as nitrites and nitrates by electric discharge.

It is well known that the formation of nitric oxide from nitrogen and oxygen takes place according to the equation :

$N_2 + O_2 + 43.2$ K Cal $= 2NO$. The nitric oxide in its turn combine with oxygen of the air and forms nitrogen peroxide, $2NO + O_2 = 2NO_2$.

The nitrogen peroxide reacts with water, and a mixture of nitric and nitrous acids according to the equation : $2NO_2 + H_2O = HNO_3 + HNO_2$ is produced. The nitrous acid, being unstable, decomposes as follows : $3HNO_2 \rightleftharpoons HNO_3 + H_2O + 2NO$; the nitric oxide, thus formed again, reacts with oxygen and forms nitrogen peroxide. In presence of alkali the following reaction takes place : $2NaOH + 2NO_2 = NaNO_2 + NaNO_3 + H_2O$.

This industrial process has a low efficiency. Assuming that 21.6 KCals. are needed for producing 30 grams or 1 mol of nitric oxide, the theoretical value per mol is 0.05 K watt hour. In practice, however, the energy required is 1 K watt hour per mol of nitric oxide formed. Thus the efficiency of this process of fixing nitrogen does not exceed 5%. Hence the arc process, which is uneconomical, has been practically abandoned except where electricity is very cheap. In practice only 1.5 to 2.5% of the gas leaving the arc at 2,500° consists of nitric oxide and cooling is necessary for combining it with oxygen.

F. 8

It is well known that the cyanamide process of nitrogen fixation is more efficient than the arc process, which requires five times more electric energy per unit of nitrogen fixed than in the former, but as cyanamide has to be converted into ammonia for industrial purposes, this method has not been generally utilised except in Germany.

The Haber-Bosch process is generally adopted at present in most countries but the yield of ammonia is usually 8% of the initial nitrogen concentration. Physicists and Industrialists have concluded that the average efficiency of the process is 10%.

Nitrogen Fixation in soils, sand etc.—For over 20 years we have studied systematically the nitrogen fixation by mixing different energy-producing materials like sugars, starch, cellulose, glycerol, fats, saw-dust, straw, leaves, peat, lignite, bituminous coal etc. with soil or sand or pure chemicals, like oxides of metals, sparingly soluble phosphates and sulphates as surfaces both in light and in the dark under sterile and unsterile conditions. Our results show that when one gram of carbon is oxidised, 10 to 25 milligrams of nitrogen is fixed in presence of sunlight in soils and in the dark the amount of nitrogen fixation is about half. In sand as a medium the efficiency, i.e., the amount of nitrogen fixed in milligrams per gram of carbon oxidised, goes upto 30 to 40 in sunlight. In nickel oxide or calcium phosphate as a medium, the efficiency is usually between 60 and 70 milligrams per gram of carbon oxidised. In sterile conditions in general the nitrogen fixation appears to be appreciably smaller than under unsterile conditions chiefly because in the process of sterilisation a part of the ammonium salts and proteins decomposes and is lost from the system.

We have already explained the larger efficiency in sand than in soil from the viewpoint that as soon as some nitrogen is fixed, a part is lost as nitrogen gas in the process of ammonification and nitrification which are also accelerated by light. These processes take place in the following manner :—

Proteins$\longrightarrow$amino acid$\xrightarrow{+O_2}$ammonia$\xrightarrow{+O_2}$nitrite$\xrightarrow{+O_2}$nitrate. In the course of these reactions, there is always the formation and decomposition of the unstable substance, ammonium nitrite, which breaks up as follows :
$NH_4NO_2 = N_2 + 2H_2O + 718$ K Cals.

Recently we have carried on a large amount of work on nitrogen fixation in artificial light from a 60 watt electric bulb. The dishes or tubes containing the reaction mixtures were placed at a distance of three feet from the bulb, whilst for dark experiments similar sets were covered with thick black cloth. For the unsterile experiments the reaction mixtures were placed in dishes and exposed to light or kept in the dark after adding 20% distilled water. The mixtures were stirred on alternate days to facilitate oxidation. After definite intervals samples were taken and analysed for their carbon, total nitrogen, ammoniacal and nitric nitrogen contents. In many experiments the Azotobacter counts were made by the plate method. The carbon and nitrogen estimations were carried on according to the method of Robinson, McLean & Williams. (J. Agric. Sci., 1929 **19**, 315). For the sterile experiments, definite weights (5 to 10 grams) of soil or other surfaces were mixed different energy materials in test tubes containing 7 to 10 c.cs of distilled water. This mixture was sterilised in an autoclave for four hours at 20 lbs. pressure. After known intervals of exposure the mixture was oven dried and an aliquot part analysed. The following results have been obtained :—

Percentage Composition of the oven-dried Soil :—

PH of the Soil	=7.5
Total Carbon	=1.5980
Total nitrogen	=0.2075
CaO	=3.4020
P_2O_5	=0.4178

Percentage Composition of the energy-materials used :—

	Wheat straw	*Gur* (Sugar Candy)
Total carbon	=39.17	36.19
Total nitrogen	=0.6375	0.7413
CaO	=0.2884	1.0010
P_2O_5	=0.0619	0.0098

Amount of phosphate added as $Na_2 HPO_4$, $12H_2 O = 2.5210$ gams. per 200 gms. soil.

Amount of Calcium Carbonate added=0.5 gram per 200 gms Soil.

TABLE 1

200 gms soil+4 grams wheat straw—*Unsterile*   *Light*

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
0	2.3343	0	0.2158	0	..
80	1.3140	1.0203	0.3866	+0.1708	167.4

200 gms soil+4 gms wheat straw   *Dark*

| 0 | 2.3343 | 0 | 0.2158 | 0 | .. |
| 80 | 1.3730 | 0.9613 | 0.3271 | +0.1117 | 116.2 |

200 gms soil+4 gms wheat straw + Phosphate   *Light*

| 0 | 2.3120 | 0 | 0.2136 | 0 | .. |
| 80 | 1.0270 | 1.2850 | 0.4163 | +0.2027 | 157.7 |

200 gms soil+4 gms wheat straw+Phosphate   *Dark*

| 0 | 2.3120 | 0 | 0.2136 | 0 | 0 |
| 80 | 1.0530 | 1.2590 | 0.3450 | +0.1314 | 104.3 |

200 gms soil+4 gms wheat straw+Calcium carbonate.   *Light*

| 0 | 2.3274 | 0 | 0.2153 | 0 | .. |
| 80 | 0.9696 | 1.3578 | 0.4245 | +0.2092 | 154.1 |

200 gms soil+4 gms wheat straw+calcium Carbonate.   *Dark*

| 0 | 2.3274 | 0 | 0.2153 | 0 | .. |
| 80 | 0.9895 | 1.3379 | 0.3732 | +0.1579 | 118 |

TABLE 2

200 gms soil+4 gms *Gur* (Sugar candy).—*Unsterile*   *Light*

| 0 | 2.2754 | 0 | 0.2209 | 0 | .. |
| 100 | 0.9560 | 1.3194 | 0.3210 | +0.1001 | 75.8 |

200 gms soil+4 gms *Gur* (Sugar candy).   *Dark*

| 0 | 2.2754 | 0 | 0.2209 | 0 | .. |
| 100 | 0.9770 | 1.2984 | 0.2695 | +0.0486 | 37.4 |

200 gms soil+4 gms *Gur* (Sugar candy)+Phosphate.   *Light*

| 0 | 2.2620 | 0 | 0.2160 | 0 | .. |
| 100 | 0.7488 | 1.5132 | 0.3270 | +0.1110 | 73.3 |

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
200 gms soil+4 gms *Gur* (Sugar candy)+Phosphate					*Dark*
0	2.2620	0	0.2160	0	..
100	0.7577	1.5043	0.2888	+0.0728	48.3
200 gms soil+4 gms *Gur* (Sugar candy)+Calcium carbonate					*Light*
0	2.2673	0	0.2172	0	..
60	1.1740	1.0933	0.3071	+0.0899	82.2
100	0.6973	1.5700	0.3825	+0.1653	105.2
200 gms soil+4 gms *Gur* (Sugar candy)+Clacium carbonate					*Dark*
0	2.2673	0	0.2172	0	..
60	1.0370	1.2303	0.2825	+0.C653	53.1
100	0.7506	1.5167	0.3071	+0.0899	59.2

TABLE 3

10 gms soil+0.2 gm wheat straw—*Sterile*					*Light*
0	2.3320	0	0.2144	0.0	..
150	2.1175	0.2145	0.2325	+0.0181	84.3
10 gms soil+0.2 gm wheat straw—Sterile					*Dark*
0	2.3320	0	0.2144	0	..
150	2.2028	0.1292	0.2200	+0.0056	43.3

TABLE 4

10 gms soil+0.2 gm *Gur* (Sugar candy)—*Sterile*					*Light*
0	2.2550	0	0.2184	0	..
150	2.0607	0.1943	0.2325	+0.0141	73.0
10 gms soil+0.2 gm *Gur* (Sugar candy)— Sterile					*Dark*
0	2.2550	0	0.2184	0	..
150	2.0814	0.1736	0.2245	+0.0061	35.1

TABLE 5

10 gms soil+0.2 gm wheat straw+Phosphate—*Sterile*					*Light*
0	2.3310	0	0.2142	0	..
150	2.1822	0.1488	0.2263	+0.0121	81.3

in grams per cent

Period of ex-posure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency

10 gms soil+0.2 gm wheat straw+Phosphate—*Sterile*					*Dark*
0	2.3310	0	0.2142	0	..
150	2.2200	0.1110	0.2185	+0.0043	38.7

·TABLE 6

10 gms soil+0.2 gm *Gur* (Sugar candy)+Phosphate—*Sterile*					*Light*
0	2.2547	0	0.2166	0	..
150	2.0610	0.1937	0.2300	+0.0134	69.2
10 gms soil+0.2 gm *Gur* (Sugar candy)+Phosphate—*Sterile*					*Dark*
0	2.2547	0	0.2166	0	..
150	2.0925	0.1622	0.2225	+0.0059	36.1

TABLE 7

200 gms soil+4 gms wheat straw.—*Unsterile*					*Light*
0	0.8980	0	0.0556	0	..
80.	0.3900	0.5080	0.0940	+0.0384	75.6
200 gms soil+4 gms wheat straw					*Dark*
0	0.8980	0	0.0556	0	..
80.	0.4494	0.4486	0.0773	+0.0217	48.3
200 gms soil+4 gms wheat straw+Phosphate					*Light*
0	0.8872	0	0.0550	0	..
80.	0.3689	0.5183	0.0942	+0.0392	65.9
200 gms soil+4 gms wheat straw+Phosphate					*Dark*
0	0.8872	0	0.0550	0	..
80.	0.3905	0.4967	0.0775	+0.0225	34.2
200 gms soil+4 gms wheat straw+Calcium carbonate.					*Light*
0	0.8958	0	0.0555	0	..
80.	0.3445	0.5513	0.0960	+0.0405	72.5
200 gms soil+4 gms wheat straw+Calcium carbonate.					*Dark*
0	0.8958	0	0.0555	0	..
80.	0.3777	0.5181	0.0802	+0.0247	47.6

In the following experiments another soil of which the carbon and nitrogen status was lower than the other one was used.

Percentage composition of the oven-dried Soil :

PH of the   Soil   =8.02
Total carbon   ,,   =0.1330
Total nitrogen   ,,   =0.0440
CaO   ,,   =2.3800
P_2O_5 ,,   =0.3385

Percentage composition of the energy materials used :—

	Wheat straw	Gur (Sugar candy)
Total carbon	=39.17	36.19
Total nitrogen	=0.6375	0.7413
CaO	=0.2884	1.0010
P_2O_5	=0.0619	0.0098

Amount of phosphate added as Na_2HPO_4, $12H_2O$=2.5210 gms. per 200 gms. Soil.

Amount of Calcium carbonate added=0.5 gram per 200 gms. Soil.

TABLE 8

200 gms soil+4 gms Gur (Sugar candy)—*Unsterile*   *Light*

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
0	0.8400	0	0.0586	0	..
100	0.2020	0.6380	0.0810	+0.0224	35.1
		200 gms soil+4 gms Gur (Sugar candy)			*Dark*
0	0.8400	0	0.0586	0	..
100	0.2084	0.6316	0.0689	+0.0103	16.3
		200 gms soil+4 gms Gur (Sugar candy)+Phosphate			*Light*
0	0.8300	0	0.0570	0	..
100	0.0499	0.7801	0.0852	+0.0282	36.1
		200 gms soil+4 gms Gur (Sugar candy)+Phosphate			*Dark*
0	0.8300	0	0.0570	0	..
100	0.0266	0.8034	0.0765	+0.0195	24.

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
200 gms soil+4 gms *Gur* (Sugar candy)+Calcium Carbonate					*Light*
0	0.8380	0	0.0575	0	..
60	0.1056	0.7324	0.0940	+0.0365	49.8
100	0.0836	0.7544	0.0948	+0.0373	49.4
200 gms soil+4 gms *Gur* (Sugar candy)+Calcium Carbonate					*Dark*
0	0.8380	0	0.0575	0	..
60	0.0874	0.7506	0.0773	+0.0198	26.3
100	0.0711	0.7669	0.0775	+0.0200	26.1

TABLE 9

	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
10 gms soil+0.2 gm wheat straw—*Sterile*					*Light*
0	0.9360	0	0.0548	0	..
150	0.7822	0.1538	0.0673	+0.0125	81.2
10 gms soil+0.2 gm wheat straw—*Srerile*					*Dark*
0	0.9360	0	0.0548	0	..
150	0.7948	0.1412	0.0605	+0.0057	40.3

TABLE 10

	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
10 gms soil+0.2 gm *Gur* (Sugar candy)—*Sterile*					*Light*
0	0.8580	0	0.0570	0	..
150	0.7125	0.1455	0.0675	+0.0105	72.1
10 gms soil+0.2 gm *Gur* (Sugar candy)—*Sterile*					*Dark*
0	0.8580	0	0.0570	0	..
150	0.7238	0.1342	0.0618	+0.0048	35.7

TABLE 11

	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
10 gms soil+0.2 gm wheat straw+Phosphate—*Sterile*					*Light*
0	0.9354	0	0.0545	0	..
150	0.7865	0.1489	0.0665	+0.0120	80.6
10 gms soil+0.2 gm wheat straw+Phosphate—*Sterile*					*Dark*
0	0.9354	0	0.0545	0	..
150	0.7970	0.1384	0.0600	+0.0055	39.7

TABLE 12

10 gms soil+0.2 gm *Gur* (Sugar candy)+Phosphate—*Sterile*   *Light*

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
0	0.8584	0	0.0565	0	..
150	0.7130	0.1454	0.0660	+0.0095	65.3

10 gms soil+0.2 gm *Gur* (Sugar candy)+Phosphate—*Sterile*   *Dark*

0	0.8584	0	0.0565	0	..
150	0.7242	0.1342	0.0608	+0.0043	32.0

In the following experiments, sand was used instead of soil. Analysis of oven dried sand used in the experiment.

Total carbon $=0.03656\%$

Total nitrogen $=0.0035\%$

CaO $=2.50\%$

P_2O_5 $=0.045\%$

PH—8.

TABLE 13

200 gms. Sand+1.3513 gms Sucrose—*Unsterile*   *Light*

In Grams percent

Period of exposure in days	Total Carbon	Amount of Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency	Azotobacter count in millions per gm.
0	0.2938	0.0	0.00475	0.0	..	0.003
60	0.0142	0.2796	0.0205	+0.01575	59.4	4.0

200 gms Sand+1.3513 gms. Sucrose—*Unsterile*   *Dark*

0	0.2938	0.0	0.00475	0.0	..	0.003
60	0.0082	0.2856	0.0150	+0.01025	35.8	91.0

200 gms Sand+1.3513 gms Sucrose+0.5%P_2O_5 as $Na_2HPO_4 2H_2O$—*Unsterile Light*

0	0.2938	0.0	0.00475	0	..	0.003
60	0.1111	0.1827	0.04125	+0.0368	199.7	0.200

F. 9

200 gms sand+1.3513 gms sucrose+0.5%P_2O_5 as $Na_2HPO_4\ 2H_2O$—*Unsterile Dark*

in grams per cent

Period of exposure in days	Total carbon	Amount of carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency	Azotobactor count in millions per gm.
0	0.2938	0.0	0.00475	0	..	0.003
60	0.0	0.2938	0.0175	+0.01275	43.4	21.0

TABLE 14

200 gms Sand+2.7027 gms Sucrose—*Unsterile*   *Light*

0	0.5237	0	0.0050	0	..	0.003
60	0.0506	0.4731	0.0240	+0.019	40.16	0.0072

200 gms Sand+2.7027 gms. Sucrose—*Unsterile*   *Dark*

0	0.5237	0	0.0050	0	..	0.003
60	0.00573	0.51797	0.01825	+0.01325	25.5	7.6

200 gms Sand+2.7027 gms Sucrose+0.5% P_2O_5 as $Na_2HPO_4\ 2H_2O$—*Unsterile Light*

0	0.5237	0	0.0050	0	..	0.003
60	0.3300	0.1937	0.0475	+0.0425	219.7	0.006

200 gms Sand+2.7027 gms Sucrose+0.5%P_2O_5 as $Na_2HPO_4\ 2H_2O$—*Unsterile Dark*

0	0.5237	0	0.0050	0	..	0.003
60	0.0199	0.5038	0.03305	+0.02805	55.6	0.080

In the following experiments another sample of sand was used.

Percentage composition of the oven dried sand used in the experiment.

PH of the sand   = 8.3
Carbon   = 0.0273
Nitrogen   = 0.00893
CaO   = 2.408
P_2O_5 = 0.0435

TABLE 15

200 grams Sand+12.5 grams Tartaric acid—*Unsterile*   *Light*

In grams per cent

Period of exposure in days	Total carbon in tartaric acid	Carbon oxidised	Total nitrogen	Change in nitrogen	Efficiency
0	2	0	0.00841	0	..
187	1.3542	0.6458	0.01786	+0.00945	14.6

200 grams Sand+12.5 grams Tartaric acid   *Dark*

in grams per cent

Period of exposure in days	Total carbon	Carbon oxidised	Total nitrogen	Change in total nitrogen	Efficiency
0	2	0	0.00841	0	..
187	1.6096	0.3904	0.0119	+0.00349	8.9

TABLE 16

200 grams Sand+11.6664 grams Citric acid   *Light*

0	2	0	0.00844	0	..
187	1.3406	0.6594	0.01563	+0.00719	10.9

200 grams Sand+11.6664 grams Citric acid   *Dark*

0	2	0	0.00844	0	..
187	1.502	0.498	0.0122	+0.00376	7.55

TABLE 17

200 grams Sand+21 grams Oxalic acid   *Light*

0	2	0	0.00808	0	...
187	1.821	0.179	0.01613	+0.00805	44.97

200 grams Sand +21 grams Oxalic acid   *Dark*

0	2	0	0.00808	0	...
187	1.8571	0.1429	0.01136	+0.00328	22.95

TABLE 18

10 grams Sand + ·625 grams Tartaric acid—*Sterile*   *Light*

0	2	0	0.00784	0	..
220	1.442	0.558	0.01136	+0.00352	6.13

10 grams Sand+625 grams Tartaric acid   *Dark*

0	2	0	0.00784	0	..
220	1.5427	0.4573	0.009	+0.00116	2.54

TABLE 19

10 grams Sand+ .5833 grams Citric acid   *Light*

0	2	0	0.00789	0	..
220	1.7857	0.2143	0.01111	+0.00322	15.02

10 grams Sand+ .5833 grams Citric acid   *Dark*

0	2	0	0.00789	0	..
220	1.9026	0.0974	0.00862	+0.00073	7.5

TABLE 20

10 grams Sand+1.05 grams Oxalic acid   *Light*

In grams percent

Period of exposure in days	Total carbon in tartaric acid	Carbon oxidised	Total nitrogen	Change in nitrogen	Efficiency
0	2	0	0.00754	0	..
220	1.9257	0.0743	0.01191	+0.00437	58.8

10 grams Sand +1·05 grams Oxalic acid   *Dark*

| 0 | 2 | 2 | 0.00754 | 0 | .. |
| 220 | 1.9657 | 0.0343 | 0.00833 | +0.00079 | 23.03 |

The foregoing results show that with aliphatic organic acids as source of energy the efficiency of nitrogen fixation in sand is smaller than with carbohydrates. It seems that with acids the nitrogen fixed may be lost. In presence of phosphates in sand as medium an efficiency of 200 mgms. of nitrogen fixed per gm. of carbon oxidised has been obtained in light. In soils fairly rich in calcium and phosphate, nitrogen fixation of the order of 150 to 75 mgms. in light in unsterile conditions and of the order of 84 to 65 under sterile conditions has been observed with wheat straw. In the dark the values vary from 80 to 35 in unsterile condition and from 43 to 32 under sterile conditions. Hence there is a marked light effect in this type of nitrogen fixation.

In culture experiments on nitrogen fixation by Azotobacter, A. Koch and S. Seydal (Centrbl. Bakt. II, **31**, 570, 1912) have reported that 70 to 80 mgms. of nitrogen are fixed by Azotobacter per gram of glucose oxidized on the second and third day of growth, and only 5 to 8 milligrams on the eighth day. Although the total amount of nitrogen fixed during the first five days is small, the process is economical only in the beginning. Similarly, J. G. Lipman (N. J. Agr. Exp. Sta. Ame. Rept. 24, 217, 1903) has obtained the following results in cultures :

Mannitol, per cent   0.1   0.2   0.5   1.0   1.5
Nitrogen fixed in milligram per gram of   10.5   8.3   6.4   4.68   3.22
  mannitol.

These results on nitrogen fixation by Azotobacter in culture media are certainly not as efficient as those obtained by us with carbohydrates and cellulose.

In recent years Dr. H. L. Jensen in Lyngby (Denmark), Dr. Stöckli in Zurich and Prof. Lemoigne in Paris have emphasised that Azotobacter does not play a big role in increasing the nitrogen status of soils. From our experiments in sterile and unsterile conditions it is clear that bacterial action is not as prominent as surface reactions in soils. Hence the existence or non-existence of bacteria should not materially affect the nitrogen status of the soil as the efficiency of nitrogen fixation is of the same order, both under sterile and unsterile conditions. It appears that the micro-biological action is vigorous either in culture media containing easily decomposable energy materials or in sewage or fermentation processes. On the other hand, if the energy materials to be utilised by the micro-organisms and the microbial population are diluted or mixed up with large quantities of inert and difficultly soluble materials like sand, soil, iron oxide, zinc oxide, nickel oxide etc., the intensity of the microbial action decreases. In most experiments for the isolation or detection of bacteria, the conditions are rendered highly suitable for their rapid multiplication by supplying energy materials for their growth and activity and mineral requirements. That is why Azotobacter or Clostridia have been found to multiply and fix nitrogen in tubes of flasks; but under natural conditions in fields the amount of nitrogen fixed by the addition of energy materials has not been accurately determined. In culture experiments in flasks containing energy materials like glucose, mannitol etc., and minerals like lime, potash, phosphate, iron etc. they are readily available to the bacteria in a state of solution. On the other hand, even if 10 tons of molasses or straw are added per acre of land, it is diluted with 99% of its weight of inert silicates, iron oxide, humus etc. present in the soil, and hence the chance of bacteria and the food materials to come in contact with each other appears to be much less than in culture media in flasks. It is clear, therefore, that the chemical changes involved in bacterial reactions with energy materials are bound to be slower in soils than in culture media, and that is why on adding organic matter to the soil, a larger time interval is necessary before the oxidation and nitrogen fixation are observed than in the culture media. This explains the failure of H. L. Jensen (Proc. Linn. Soc. N. S. W. 1940, 65,1) to observe nitrogen fixation in many samples of New South Wales soils during an incubation period

of 30 days when mixed with glucose as energy material. It appears that the nitrogen fixation in 30 days in soils is much less than in culture media containing glucose. In cold countries the soil nitrogen fixation is slower than in warm countries. Moreover, in cold countries the nitrogen status of soils is higher than in warm countries, and the apparent nitrogen fixation on adding energy materials is less prominent than in hot countries.

By the application of three doses of Neem Leaf (Melia Azadiractta Lina) to field soils containing 0.0386% total nitrogen, the nitrogen status was raised to 0.1025% by nitrogen fixation and the carbon-nitrogen ratio of the soil became 10. Similarly, by adding cowdung three times, the nitrogen status could be raised to 0.2% in 3 years from 0.0386%. Moreover, on applying municipal rubbish the nitrogen status was raised to 0.25% from 0.039%, and bumper crops were grown on this land. The classical Rothamsted experiments show that by adding farmyard manure at the rate of 14 tons per acre per year and growing a crop every year on this land, the nitrogen status was raised to 0.256% from 0.122%. Similar experiments carried on with farmyard manure in Denmark showed the following increase of the soil nitrogen :—

		Increase with farmyard manure	Increase with artificial fertilizers
Sandy soil	0.066% N	30.3%	15.1%
Lyngby soil	0.146% N	15.7%	3.4%
Askov Loam	0.106% N	22.6%	11.3%
Lundgard	0.106% N	10.3%	3.7%
Tylstrup	0.118% N	6.1%	1.6%

Moreover, we have been able to show definitely that marked nitrogen fixation takes place under completely sterile conditions, both in light and dark. Hence it appears that the nitrogen status of soils of all countries not under legumes appears to be chiefly due to surface and photo-oxidation of all kinds of energy materials and consequent nitrogen fixation.

Mechanism of Nitrogen Fixation.—In explaining photo-synthesis in plants, Dhar postulated in 1933 that the important photo-chemical reaction is the decomposition of water by absorption of light according to the following equation :—

$$H_2O + 112 \; K \; Cal = H + OH.$$

The hydrogen atom thus formed reduces the carbonic acid adsorbed on the leaves forming formaldehyde. In recent years this view of the mechanism of photosynthesis has been supported by the use of carbonic acid containing isotopic carbon. In explaining nitrogen fixation the best mechanism seems to be the same, i.e. the decomposition of water into H and OH by absorption of energy obtained from the oxidation of carbohydrates, celluloses, lignin, fats, coals etc. Moreover, in presence of light, the light energy, whether from the sun or artificial source, is absorbed by the system and utilised in increasing nitrogen fixation. In symbiotic nitrogen fixation also the same machanism may be applicable.

For fixing 14 gms. of nitrogen and forming ammonia by the interaction of molecular nitrogen and atomic hydrogen obtained by the decomposition of water as stated above, 336 K cal. are needed. Hence, from the oxidation of a gram mol of glucose according to the equation

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 676 \text{ K. Cal. } \frac{14 \times 676}{336} \text{ grs. of nitrogen}$$

can be fixed under ideal conditions. In other words, 0.39 gram of nitrogen should be fixed per gram of carbon oxidised. In many of our experiments in soils, fairly rich in calcium and phosphate, a nitrogen fixation of 100 mgms. with sugar candy and about 150 with wheat straw has been observed per gram of carbon oxidised. Hence the efficiency of this type of nitrogen fixation in soils is $150/390 \times 100 = 38\%$ with straw in light, and with sugar candy $100/390 \times 100 = 25\%$. In sterile conditions the efficiency in light is 21% with wheat straw; in the dark this efficiency is 10%.

It is well known that in absence of moisture nitrogen fixation in soils does not take place, because water plays a prominent part as postulated in the mechanism of nitrogen fixation proposed above. The ammonia can readily be oxidised to nitrates in soils or nodules. Dhar and Mukherji (J. Indian Chem. Soc., 1934, 11, 727) have obtained amino acids readily by the action of nitrates on carbohydrates in presence of light using titania as a photo catalyst. In symbiotic nitrogen fixation the energy required is supplied by the oxidation of the carbohydrates photosynthesised by the host plant and nitrogen fixation takes place chiefly in the nodules. In this process the possibility of the loss of nitrogen by the formation and decomposition of the ammonium nitrite appears to be less than in our

experiments where the facility for the oxidation of proteins, amino acids, ammonium salts obtained by fixation, is greater than in nodules. This is certainly one of the reasons why symbiotic nitrogen fixation frequently appears to be more efficient than non symbiotic fixation.

Ammonia is readily detected in nitrogen fixation by Azotobacter or Clostridia in culture media. In our experiments on nitrogen fixation in sand or soil with soluble carbohydrates or glycerol as energy materials, there is marked increase of ammonical nitrogen in a short time. Moreover using *sanai* (sun hemp) as energy material in nitrogen fixation we have frequently observed a pronounced smell of free ammonia when the nodules are rubbed under fingers.

It is well known that in symbiotic or non-symbiotic nitrogen fixation there is hardly any increase of nitrogen in presence of small amount of ammonium salt or nitrate. Similarly in our experiments the nitrogen, fixation falls off on the addition of ammonium salts. This is due to the fact that the fixation is opposed by the phenomenon of loss of nitrogen involved in nitrification caused by the formation and decomposition of the unstable substance ammonium nitrite. This loss is retarded by the presence of carbohydrates which act as a negative catalysts in nitrification. It appears that the fundamental chemical changes involved in all types of nitrogen fixation are identical. In symbiotic fixation the Rhizobia containing haemoglobin may be able to oxidize the carbohydrates synthesized by the host plant very readily creating an efficient nitrogen fixation process, which certainly requires an influx of energy. Also Phosphates and calcium carbonate seem to increase the efficiency of nitrogen fixation in all types of nitrogen fixation, in which ammonia formation is an important step.

Efficiency of Symbiotic Nitrogen Fixation

P. W. Wilson (Biochemistry of Nitrogen Fixation, Madison, 1940) has reported that in nitrogen fixation by red clover using sucrose in sand culture, a nitrogen fixation of 1 gram has been obtained per 25 grams of dry plant material. Assuming that 40% of this plant material is carbon, the symbiotic nitrogen fixation by red clover becomes 100 mgms. per gram of carbon oxidised in symbiosis. It is very interesting, therefore, that the efficiency of symbiotic nitrogen fixation, which has always been

considered to be about 10 times greater than that of non-symbiotic fixation, may be even smaller than the efficiency obtained in light in our experiments. In the manuring of fields with legumes, Weir has stated that under normal conditions 1 cwt., i. e. 112 lbs. of nitrogen, are added per acre, but usually the amount may be as small as 40-60 lbs. On the other hand, when 5-10 tons of leaves or straw are added to the soil, rich in calcium phosphate specially in tropical countries, the nitrogen addition may be much greater than with legumes. Moreover, legumes cannot be grown year after year in the same soil. Also, legumes make the soil certainly more acidic than straw or plant leaf and are known to be an acidic manure. It seems, therefore, that there is very little to choose between legume manuring and carbohydrate manuring. The carbohydrate manuring or lignite manuring is specially suitable in soil containing low total nitrogen and neutral type rich in calcium phosphate. Recent experiments carried on in Nigeria with 1 ton of farm yard manure per acre have produced excellent results in crop production, because of the low nitrogen content of the soil. This is in support of our observations and conclusions. In cold countries carbohydrate and lignite manuring should be quite suitable in presence of calcium carbonate or calcium phosphate as our experiments show that in the presence of calcium carbonate the oxidation of both, carbohydrate and straw, is intensified in nitrogen fixation.

As the industrial methods of nitrogen fixation are not very efficient, the price of artificially fixed nitrogen has remained high. The world production of this commodity in 1937 was 3.54 million tons. Even today the total production may not exceed 4 or 5 million tons. For producing 600 million tons of cereals and 400 million tons of good food material (these are the amounts produced at present in the world) no less than 150 million tons of combined nitrogen are needed. Hence synthetic nitrogen has failed to cope with world food production. It is no wonder, therefore, that in the 1949 Meeting of the British Accociation, it was concluded that only 3% of the world food production has to be attributed to synthetic nitrogen and 97% of the food is derived from the nitrogen of the soil humus. It is clear, therefore, that nitrogen fixation in soil has to improve markedly not only by growing legumes as is being done in all the advanced countries, but nitrogen fixation in presence of sunlight by addition of all kinds of

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energy materials to the soil has to be intensified, because organic matter not only supplies the minerals and nitrogen it contains but also fixes atmospheric nitrogen readily in the soil and protects the soil nitrogen from loss in the gaseous state.

It is interesting to note that the immortal Chemist, Lavoisier, was much impressed by the value of grass in land improvement. Recently, T. L. Lyon and H. O. Buckman (The Nature & Properties of Soils, New York, 1943, 393) at Ithaca, have reported that the soil under a grass ley free from legumes gained 40 lbs. of nitrogen per acre per year. Similarly, J. W. White, F. J. Holben and A. C. Richer (J. Amer. Soc. Agron., 1945 37, 21) in Pennsylvania observed that the soil under a grass ley not containing legumes, gained 15-30 lbs. of nitrogen annually, even though they were unable to isolate Azotobacter from the soil. Similar gains in nitrogen of grasslands have been reported in Rothamsted.

It appears that the carbonaceous matter added to the soil as plant parts or farmyard manure are oxidised thermally and photochemically on the soil surface and lead to nitrogen fixation even in absence of leguminous plants or Azotobacter.

In a recent paper, A. Demolon (Rev. Gen. Botanique, 58, 1951, 489) has concluded that the symbiotic fixation of nitrogen has to be enhanced by controlling and improving the processes of this fixation. We are trying to intensify the growth of leguminous plants by adding straw, leaves, farmyard manure etc. along with calcium phosphate to the soil before growing these plants.

SUMMARY

Experimental results on the influence of light from a 60 watt electric bulb show that marked nitrogen fixation takes place when soils fairly rich in calcium and phosphate are mixed with wheat straw or *gur* (sugar candy) and allowed to undergo slow oxidation in air. The amounts of nitrogen fixed in milligrams per gram of carbon oxidised are of the order of 150 to 75 in electric light under unsterile condition with wheat straw; in the dark, the fixation is 80 to 35. In sterile condition in light it is 85 to 65 and 43 to 32 in the dark.

With *gur* (sugar candy) the values can be as high as 105 in light

and 59 in the dark under unsterile conditions, whilst in sterile condition they are 69 and 56.

In unsterile condition, with sand as medium and sucrose as energy material and in presence of phosphate, the high value of 219 in light and 55 in dark was obtained.

These nitrogen fixations in light are as high as those obtained in symbiotic nitrogen fixation. Aliphatic organic acids when mixed with sand and allowed to undergo oxidation in air can fix appreciable amounts of nitrogen, both under sterile and unsterile conditions.

It has been postulated that the main chemical change involved in nitrogen fixation, as in photosynthesis in plants, is the decomposition of water into H and OH according to the equation : $H_2O + 112 \text{ K Cal} = H + OH$. The energy of the oxidation of carbohydrates and other oxidizable materials is utilised in the breaking up of water molecules into atomic hydrogen and hydroxyl radical. The atomic hydrogen thus formed can reduce molecular nitrogen to ammonia. The fundamental chemical changes in all types of nitrogen fixation involve the production of ammonia and seem identical.

It appears that the efficiencies of the industrial methods of fixing atmospheric nitrogen are lower than those occurring in soils and sands in presence of organic matter and calcium phosphate aided by light absorption and in leguminous plants. It seems that the lower efficiency of industrial nitrogen fixation explains why synthetic nitrogen is unable to cope with the world food production.

Straw, leaves, farmyard manure etc. can not only fix atmospheric nitrogen in soil and protect the soil nitrogen but can also intensify the growth of legumes in soils.

The surface oxidation of energy materials when added to soils can become more prominent in presence of light than microbial oxidation of energy materials.

Recent field trials showing the increase of nitrogen in land covered with grass but not containing legumes and Azotobacter are in agreement with our conclusions that plant parts, farmyard manure and other organic matter can be oxidised thermally and photochemically even in absence of Azotobacter or legumes and lead to nitrogen fixation.

NEW ASPECTS OF THE VALUE OF PHOSPHATES AND CARBONATES IN LAND FERTILITY

BY N. R. DHAR

The parts played by phosphates in the soil seem to require further clarification. There is no doubt that phosphates are needed by plants and micro-organisms for their cell formation, respiration etc. and naturally their presence intensifies the growth of plants and microbial cells.

On the other hand, there are certain chemical and physico-chemical processes taking place in the soil on the addition of phosphates, which require further consideration.

BUFFERING EFFECT OF PHOSPHATES AND CARBONATES

It is well known that carbonic acid is a much weaker acid than phosphoric acid as is evident from their dissociation constants :—

Carbonic Acid : H_2CO_3 : dissociation constant $= 3 \times 10^{-7}$

$$\frac{H^\circ \times HCO_3'}{H_2CO_3} = 3 \times 10^{-7} \text{ (first dissociation constant)}$$

$$\frac{H^\circ \times CO_3''}{HCO_3'} = 6 \times 10^{-11} \text{ (second dissociation constant)}$$

Phosphoric Acid : H_3PO_4 : dissociation constant 9×10^{-3}

$$\frac{H^\circ \times H_2PO_4'}{H_3PO_4} = 1.1 \times 10^{-2} \text{ (first dissociation constant)}$$

$$\frac{H^\circ \times HPO_4''}{H_2PO_4'} = 2 \times 10^{-7} \text{ (second dissociation constant)}$$

$$\frac{H^\circ \times PO_4'''}{HPO_4''} = 3.6 \times 10^{-13} \text{ (third dissociation constant)}$$

That is why calcium carbonate, of which the solubility is practically the same as that of calcium phosphate, is more alkaline towards indicators

than calcium phosphate. The solubilities of some of these substances are recorded below :—

Substance	Formula	Solubility in 100 parts of water at 0°C.
Calcium Carbonate.	$CaCO_3$	0.0013
Dicalcium Phosphate	$Ca_2H_2 (PO_4)_2 2H_2O.$	0.028
Magnesium Carbonate	$MgCO_3$	0.0106
Monocalcium Phosphate	$CaH_4 (PO_4)_2 H_2O$	4.0....at 15°C.
Tricalcium Phosphate	$Ca_3 (PO_4)_2$	0.0013

Moreover, we have observed that when tricalcium phosphate is boiled with distilled water and the mixture filtered an appreciable amount of phosphoric acid is dissolved, and can be estimated as phosphomolybdate, because the following hydrolysis reactions take place :—

1. $Ca_3 (PO_4)_2 + 2H_2O = 2CaHPO_4 + Ca (OH)_2$

2. $Ca_3 (PO_4)_2 + 4H_2O = Ca (H_2PO_4)_2 + 2Ca (OH)_2$

3. $Ca_3 (PO_4)_2 + 6H_2O = 2H_3PO_4 + 3Ca(OH)_2$

In the soil solution such hydrolysis reaction can also take place and phosphates are made available to crops slowly. Because the second and third dissociation constants of phosphoric acid are small, whenever hydrogen ions are available in the soil solution along with phosphate ions, HPO_4'' and H_2PO_4' ions are readily formed and hence the hydrogen ion concentration in the system decreases. Similarly as the first and second dissociation constants of carbonic acid are also small, carbonate and bicarbonate ions present in the soil solution readily combine with hydrogen ions and form carbonic acid. Thus phosphates and carbonates can act as excellent buffers in the soil.

It seems that both liming and addition of phosphates are more important to temperate country soils, which are on the acidic side, than to tropical soils, which are on the alkaline side.

Moreover, when dicalcium or tricalcium or magnesium phosphate is added to acidic soils containing aluminium, iron and titanium phosphates of which the solubility products are smaller than those of tricalcium or

magnesium phosphates, the hydrogen ions are removed readily and H_2PO_4' and HPO_4'' are formed for the benefit of crops. On liming these soils, the hydrogen ions are also removed readily due to the formation of bicarbonate and carbonic acid. The lime further acts according to the law of mass action on the phosphates of aluminium, iron and titanium forming hydroxides of these metals and calcium phosphate which is more readily available to plants than the other less soluble phosphates. In this way liming decreases the phosphate consumption in the soil. Similarly phosphates, by removing hydrogen ions from soil, decrease the lime consumption of soils. In this respect the function of phosphates is certainly of the same type as that of calcium and magnesium carbonates. There is no doubt, therefore, that addition of phosphates and addition of carbonates of calcium and magnesium or lime, perform the same function in the soil, that is, removal of hydrogen ions or acidity. It is, therefore, clear that addition of phosphates decreases the need of liming or *vice-versa*. This important conclusion has been supported by the following results :—

	Total crop grown during 5 years (Tons)	Lime requirement Jones method, Lbs. CaO per acre
No Phosphate	17.6	2700
Phosphate rocks	29.4	2520
Superphosphates	31.5	2340
Extra superphosphate	42.2	2250
Ground bone	33.4	2160
Thomas slag	32.7	2070

In Collings' book on "Commercial Fertilizers" it has been stated on page 217 that the American people are the greatest producers, consumers and wasters of phosphates. As the majority of the land under cultivation in the U. S. A. and Europe is on the acidic side, addition of phosphates is certainly beneficial, because they act as buffer and remove the acidity of soils even without liming. Over-liming does harm to the soil, but over-phosphating has never been reported to be harmful to plants or soils.

NITROGEN FIXATION IN SOILS BY ADDING LIME, CALCIUM CARBONATE OR PHOSPHATES

It is certain that liming and the addition of phosphates decrease the acidity of soils and favour the oxidation of the organic substances present therein. It is well known that the carbon nitrogen ratio of soils increases with their acidity. On the other hand, we have repeatedly observed that the carbon nitrogen ratio of alkali soils is much smaller than 10. Frequently, this ratio in the alkali soils of India having a pH of 10.7 is three. In other words, the percentage of nitrogen present in the humus of the soil depends on the pH of the soil. The greater the pH, the greater is the percentage of nitrogen present in the humus of the soil. Hence, it can be inferred that on adding lime or calcium carbonate to an acid soil, not only the acidity decreases but also the carbonaceous matter undergoes more rapid oxidation, and the energy obtained in this oxidation fixes the nitrogen of the atmosphere in the soil. Thus, the carbon-nitrogen ratio of the acid soil decreases and its fertility increases. These conclusions are supported by the properties of fen soils. Russell has reported that when the vegetation includes calcicolous (calcium rich) plants, neutral humus soils, in which the oxidation of the organic matter is rapid, are formed. The chief characteristics of these fen soils are their richness in lime and high nitrogen content (3%). When drained, these fen soils prove highly fertile. The soil water is not acid but contains calcium bicarbonate. These soils contain calcium carbonate and hence can fix atmospheric nitrogen readily by the oxidation of organic matter, and that is why they are rich in nitrogen. They do not require nitrogen or lime but respond to phosphates.

Similarly, phosphates, which act as buffers and reduce the acidity of soils and cause an increased oxidation of the carbonaceous substances, lead to increased nitrogen fixation in the soil. In this respect liming and addition of phosphates are likely to play the same role. Recently we have observed that the efficiency of nitrogen fixation greatly increases both in normal and alkali soils by the addition of phosphates.

Value of Dicalcium Phosphate as a Buffer and a Fertilizer

It is interesting to note that when sulphuric acid reacts with calcium phosphate in the manufacture of superphosphates in the proportion of 310 parts by weight of finely-ground phosphate and 196 parts of sulphuric acid and 90 parts of water & filtered, it gives 3/4th of the total phosphoric acid as free acid. If the jelly is left to become dry and hard, the filtrate, when the mass is beaten up with water and filtered, contains monocalcium phosphate. If the quantity of the sulphuric acid is not sufficient for complete decomposition, the dicalcium salt is formed. This arises, no doubt, by the formation of the monocalcium salt and its interaction with tricalcium compound :

$$Ca_3 (PO_4)_2 + Ca (H_2PO_4)_2 = 2Ca_2 (HPO_4)_2$$
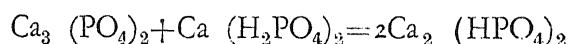
This represents one phase of the so-called reversion of the phosphoric acid. When there is an excess of sulphuric acid, there is a complete decomposition of the calcium salts and liberation of free phosphoric acid, which is harmful to the soil, specially in large concentrations.

The average composition of a sample of superphosphate is as follows :—

	percent
Gypsum (Ca SO_4 . $2H_2O$)	50.00
Monocalcium phosphate ($CaH_4 (PO_4)_2$. H_2O)	26.60
Dicalcium phosphate ($Ca_2H_2 (PO_4)_2$. H_2O)	2.40
Tricalcium phosphate ($Ca_3 (PO_4)_2$)	2.20
Silica (SiO_2)	7.00
Iron & Aluminium sulphates ($Fe_2 (SO_4)_3 + (Al_2 (SO_4)_3$)	4.00
Calcium Fluoride (CaF_2)	1.50
Water (H_2O)	6.00

The following table shows the proportion of various phosphate ions in the solution per 100 mols of dissolved phosphates in different pH values :—

pH.	4	5	6	7	8	9
Mols of H_3PO_4	0.9	0.1	8×10^{-3}	3×10^{-4}	4×10^{-6}	5×10^{-8}
Mols of H_2PO_4'	98.9	98	82	33	3	0.5
Mols of HPO_4''	0.2	2	18	67	97	99.5
Mols of PO_4'''	7×10^{-10}	7×10^{-8}	6×10^{-6}	2×10^{-4}	3×10^{-3}	4×10^{-2}

It is clear, therefore, that in acid soils of temperate climatic countries H_2PO_4' ions are likely to be present in larger amounts than HPO_4'' and PO_4'' ions, but in alkaline soils or even in neutral soils HPO_4'' ions are in larger amounts than H_2PO_4' ions, but because the solubility product of dicalcium hydrogen phosphate is much smaller than that of monocalcium phosphate, dicalcium hydrogen phosphate will precipitate out readily in neutral and alkaline soils in presence of Ca ions.

Moreover, the amount of monocalcium phosphate is about 12 times greater than dicalcium and tricalcium phosphate in ordinary samples of superphosphate, but in neutral and alkaline soils the monocalcium phosphate cannot remain long in soil as such but will revert to the dicalcium and tricalcium phosphates. Hence, it seems unprofitable to add superphosphate to our soils.

If tricalcium and dicalcium phosphates are added to the acidic soils of temperate climate, monocalcium phosphate is likely to be formed and this is as good as adding superphosphate or even better than superphosphate because the pH goes up on the addition of tricalcium phosphate. It seems that in alkaline or neutral soils of tropical countries addition of sodium-hydrogen phosphate, if it can be cheaply manufactured, will be better than adding calcium phosphate, because in soils of pH7 of more, the HPO_4'' ion is much more stable than H_2PO_4' ion or PO_4''' ions.

It is clear, therefore, that the problem of fertilizing Indian soils or other tropical soils from the phosphate point of view is more complicated than in temperate country soils which are on acidic side. Quantitative experiments are necessary to find out the velocity with which calcium carbonate can react with monocalcium phosphate forming dicalcium and tricalcium phosphates. Similarly, the velocity with which tricalcium phosphate can react with monocalcium phosphate forming dicalcium phosphate has to be determined.

Hence, in the West an attempt should be made to prepare superphosphate with smaller quantities of sulphuric acid, that is, rather prepare a mixture of almost equal parts of calciummono and diphosphates and thus save a part of the cost of the sulphuric acid. In the East also dicalcium phosphate should be more profitable than the ordinary superphosphate.

F. 11

The above conclusion that dicalcium phosphate, which is less acidic than the monocalcium compound which is the chief ingredient of the super-phosphate, should be prepared in larger amounts and more used in agriculture, is supported strongly by the following experimental observations in U. S. A. :—

Availibility of Phosphates to Plants Grown in Sand

Compounds		Tomatoes	Potatoes	Lime Beans
Iron phosphate	..	1	14	52
Aluminium phosphate	..	24	90	98
Manganese phosphate	..	83	122	0
Tricalcium phosphate	..	145	110	87
Trimagnesium phosphate	..	301	320	319
Dicalcium phosphate	...	296	302	307
Monocalcium phosphate	...	320	307	371
Rock phosphate	..	5	31	33

Relative Value of various Phosphates for Crops in Kentucky

Phosphates		In Green House	IN FIELD	
			Not limed	Limed
Ordinary superphosphate	...	100	100	116
Triple superphosphate	..	94	97	119
Monocalcium phosphate ⎫ Dicalcium phosphate ⎬	...	101	100	116
Calcium metaphosphate	..	103	110	126
Fused-rock phosphate	..	100	114	126
Tricalcium phosphate	..	77	95	92
Rock phosphate	..	11	71	36
Colloidal phosphate	..	18	..	...

The foregoing results show clearly that the availability and value as a fertilizer of dicalcium phosphate is as good as monocalcium phosphate. Phosphate rock ($3Ca_3 (PO_4)_2 CaF_2$) does not react readily as it is much less soluble than $Ca_3 (PO_4)_2$ due to the presence of CaF_2.

In recent years superphosphates have been largely ammoniated and this is certainly a very desirable improvement as it increases the amount

of dicalcium phosphate and tricalcium phosphate in the superphosphate as is evident from the following table :—

Compound	Percentage with per cent Ammonia added as indicated						
	0.0	1.0	2.0	3.0	4.0	5.0	6.0
$Ca\ H_4\ (PO_4)_2$	25.0	14.3	3.5	0.0	0.0	0.0	0.0
$Ca\ H_2\ (PO_4)_2$	4.5	9.5	12.0	11.2	5.0	0.0	0.0
$Ca_3\ (PO_4)_2$	0.0	0.0	0.0	8.2	17.5	25.7	30.6
$NH_4\ H_2\ PO_4$	0.0	8.9	14.3	15.5	12.5	9.1	6.0
$(NH_4)_2\ SO_4$	0.0	0.0	0.0	2.7	8.5	14.3	20.0
$Ca\ SO_4\ .\ 2H_2O$	62.2	62.0	62.0	58.3	51.0	42.0	32.0
Inerts	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Totals	94.5	97.7	94.8	98.9	97.5	94.1	91.6

The following observations of Lohnis and Fred for four years showing that the recovery of plant food materials can be greater in the case of phosphate and potash than with nitrogen are in support of the view that phosphates can accumulate in the soil and show a residual effect :—
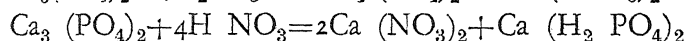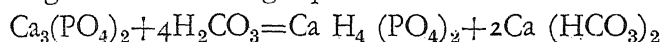
Nitrogen P_2O_5 K_2O
7.8 to 46.1%   10.1 to 75.6%   22.4 to 85.1%

Under the present practice of the fertilizer application in most advanced countries more phosphate is added to the soil than is removed by crops and lost by leaching. This is certainly a healthy step in controlling the soil acidity.

It is well known that organic matter undergoes oxidation in the soil forming carbonic acid. Moreover, there is formation of nitrous acid (dissociation constant 6×10^{-4}) and nitric acid in soils when nitrogenous compounds undergo ammonification and nitrification. When carbonic acid is passed into water-containing tricalcium phosphate in suspension, the formation of dicalcium-hydrogen-phosphate has been reported. An aqueous solution of carbondioxide in contact with normal calcium phosphate contains the following :—

CO_2 1.95   3.91   7.81   15.63 millimol/litre.
CaO   0.11   0.10   0.17   0.44 gms./litre
P_2O_5 3.32   2.90   1.77   3.30 gms./litre

Hence, phosphate rock and other sparingly-soluble calcium phosphates are made available to plants by the oxidation of organic matter in soil according to the following equation :—

$$Ca_3(PO_4)_2 + 4H_2CO_3 = Ca\ H_4\ (PO_4)_2 + 2Ca\ (HCO_3)_2$$

$$Ca_3\ (PO_4)_2 + 4H\ NO_3 = 2Ca\ (NO_3)_2 + Ca\ (H_2\ PO_4)_2$$

Ground phosphates, when mixed with farmyard manure or green manure, are acted upon as above, and the phosphate is made available to crops. Peaty soils, which are usually acidic, are frequently treated with phosphate rock with good results. Hence, a mixture of sparingly soluble phosphates with organic matter is of great value to soils. Moreover, the colloids obtained from the organic matter may hinder the reversion of soluble phosphates in the soil. As with other manures and fertilizers usually, the best results are secured from the slowly available phosphates when they are applied to crops with a long growing season or with biennial or perennial rather than annual. It seems desirable that readily availiable forms of phosphorus have to be added to crops with a short growing season.

SUMMARY

1. Calcium phosphates not only supply calcium and phosphate ions to crops but they can also act as buffers like calcium carbonate in decreasing acidity of soils.

2. On liming an acid soil the oxidation of the carbonaceous compounds is increased, and in this process the carbon-nitrogen ratio of a soil decreases and nitrogen of the air is fixed and increases the soil fertility. Phosphates play the same role. The large amount of nitrogen present in fen soils is likely to be due to the fixation of atmospheric nitrogen taking place in calcium carbonate rich soils.

3. In presence of phosphates the lime requirement of soils decreases.

4. The dicalcium phosphate should be more profitable to acid soils than the ordinary superphosphate containing monocalcium phosphate. Hence superphosphates containing more dicalcium phosphate should be manufactured with smaller quantities of sulphuric acid.

5. The accumulation of phosphates in soils is frequently observed in modern fertilizer practice and should be encouraged as it reduces the acidity of soils and helps nitrogen fixation.

6. Addition of organic matter with calcium phosphates is certainly useful as it increases the availability of phosphate. Moreover, organic matter forming colloidal substances can retard the progress of reversion of soluble phosphates.

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